

# RUBBER CHEMISTRY AND TECHNOLOGY

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## RUBBER CHEMISTRY AND TECHNOLOGY

RUBBER CHEMISTRY AND TECHNOLOGY is published quarterly under the supervision of the Editor representing the Rubber Division of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

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All applications for regular or for associate membership in the Rubber Division with its privilege of receiving this publication, all correspondence about subscriptions, back numbers, changes of address, and missing numbers, and all other information or questions should be directed to the Secretary-Treasurer of the Rubber Division, C. W. Christensen, Monsanto Chemical Company, 1012 Second National Building, Akron, Ohio.

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# Rubber Division Activities

## The Rubber Division of the American Chemical Society

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Sergeant-at-Arms.....L. V. COOPER

### The Rubber Division Meeting at Chapel Hill, North Carolina, April 14-15, 1937

The meeting was held in Manning Hall on the campus of the University of North Carolina, with one hundred-forty in attendance. The following papers were presented:

1. W. F. Tuley, Naugatuck Chemical Company. The Frosting of Vulcanized Rubber.
2. A. H. Nellen, Lee Tire and Rubber Company. The Effect of Temperature and Mill-Roll Opening on the Extrusion Qualities of Rubber.
3. A. R. Kemp and J. H. Ingmanson, Bell Telephone Laboratories, Inc. High-Speed Vulcanization of Rubber.
4. Harold Gray, Chairman, Crude Rubber Committee. Report.
5. E. W. Oldham and J. G. Harrison, Jr., The Firestone Tire and Rubber Co. Notes on the Determination of Free Carbon in Rubber Goods.
6. Felix L. Yerzley, E. I. du Pont de Nemours & Co. An Apparatus for the Evaluation of Rubber and Rubber-Like Compositions as Vibration Absorbers.
7. S. D. Gehman and J. E. Field, The Goodyear Tire and Rubber Company. Colloidal Structure of Rubber in Solution.
8. A. R. Kemp, Bell Telephone Laboratories, Inc. Purified Rubber for Electrical Insulation.
9. John T. Blake and Philip R. Bruce, Simplex Wire and Cable Co. Unsaturation of Rubber Vulcanized with Nitro Compounds and Benzoyl Peroxide.
10. D. L. Gamble and C. E. Barnett, The New Jersey Zinc Co. Scattering in the Near Infra-Red as a Measure of Particle Size and Size Distribution.
11. J. H. Fielding, The Goodyear Tire and Rubber Company. Impact Resistance in the Testing of Channel Black.
12. Howard W. Starkweather and Herbert W. Walker, E. I. du Pont de Nemours & Co. Influence of Metallic Oxides on Certain Physical Properties of Neoprene.
13. W. J. Clapson, The Eagle-Picher Lead Company. Litharge as Accelerator for Chloroprene Plastic Polymer.
14. George J. Albertoni, The Goodyear Tire and Rubber Co. Rebound-Pendulum Machine for Determining the Elastic Efficiency of Rubber.

The Rubber Division was glad to welcome Mr. Jean Le Bras at the meeting. Mr. Le Bras represented the newly organized French Institute of Rubber.

The Rubber Division Banquet was held Wednesday evening, April 14, at the Chapel Hill Country Club, with one hundred thirty-five in attendance. The Banquet Committee, consisting of C. P. Hall, A. E. Warner and Chas. Park, is to be congratulated for the dinner and entertainment.

At the close of the papers Thursday noon, a general business session was held.

R. P. Dinsmore, Chairman of the Committee on the International Rubber Conference, to be held in London in 1938, reported that twenty-two members of the Rubber Division plan to attend. Nine have agreed to prepare papers, even if they cannot attend. Mr. Dinsmore recommended that a special committee on papers be appointed to review the papers submitted for presentation at the International Conference. This recommendation was accepted, and the first Committee was disbanded.

It was voted that the Editor and Advertising Manager of Rubber Chemistry and Technology be members *ex officio* of the Executive Committee.

### Secretary's Report

Total Membership to date March 30, 1937.....	501
Members paid for 1937.....	404
Associate Members paid for 1937.....	97
New members and Associate Members for 1937 (included in above figure).....	51
Total membership not paid for 1937.....	44
Members not paid for 1937.....	26
Associate members not paid for 1937.....	18
New members for 1936 who did not renew membership for 1937.....	19
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The Secretary reported that he had sold a one-half interest in the loud speaker, owned by the Rubber Division, to the Akron Section of the American Chemical Society.

The Secretary also brought up the idea of having our programs planographed along the lines used by some of the other divisions. This was felt to be a needless expense, in view of the fact that our abstracts are printed, before our Meetings, in the *India Rubber World* and *The Rubber Age*.

The Secretary reported that he had corresponded with the *India Rubber Journal* with a view to obtaining copies of "Gum Elastic" by Goodyear, to be given to the Members in 1939. In view of the price, \$3.64 per copy for 250 copies or more, the idea was given up.

C. W. CHRISTENSEN, *Secretary-Treasurer*

# Chemical Aspects of Vulcanization

A. van Rossem

RIJKS RUBBERDIENST, DELFT, HOLLAND

C. O. Weber<sup>1</sup> was the first to give an elaborate theory of vulcanization. It is well known that he considered the hot vulcanization process as an addition of sulfur to polyprene ( $C_{10}H_{16}$ )<sub>n</sub> on account of the fact that no large amounts of hydrogen sulfide were evolved during the process.

Wo. Ostwald,<sup>2</sup> starting from quite the opposite point of view to Weber, put forward in 1910 the adsorption theory of vulcanization, considering it from an entirely colloidal standpoint, the sulfur being adsorbed by the rubber.

It soon became clear that vulcanization was much more complex, and that neither of the two theories was able to explain the facts. Since then many investigations have been carried out, and many views, hypotheses, and theories on vulcanization put forward. If one tries to classify these, it becomes apparent that at the present time there is still a chemical theory and a colloidal theory of vulcanization.

The chemical theory of vulcanization may be divided in two opposing hypotheses, *viz.*:

(a) Polymerization of the rubber molecule, combination with sulfur being incidental.

(b) Chemical combination of sulfur with rubber as the principal factor.

To support this statement a few references and quotations from various investigators are given below.

## (a) Polymerization Theories

Hauser<sup>3</sup> was of the opinion that no reaction between sulfur and rubber is needed to achieve the effect which we call vulcanization, the chemical combination of sulfur and rubber being a secondary effect only. In his opinion polymerization of the rubber is the primary factor in vulcanization.

Schidrowitz,<sup>4</sup> in one of his weekly reviews, wrote: "I imagine that the great majority of rubber chemists, I will not speak for the physicists, nowadays look upon vulcanization as a physical process, and regard the binding of sulfur by the molecule as incidental and not characteristic."

Whitby<sup>5</sup> looks upon vulcanization as a polymerization process of the rubber. "We arrive at the conclusion that the vulcanization of rubber involves polymerization as an essential feature, and that vulcanization accelerators can act as catalyst in the polymerization."

## (b) Chemical Combination with Sulfur

Boggs and Blake<sup>6</sup> have put forward a theory which in principle considers vulcanization as the chemical addition of sulfur to the rubber molecule. The authors summarize their view as follows:

"1. Vulcanization of rubber is a chemical reaction in which the vulcanizing agent adds to all or a portion of the double bonds of the rubber molecule.

2. There are two possible stable addition products of vulcanizing agents and rubber—soft vulcanized rubber and ebonite.

3. There are two types of chemical unsaturation in the rubber molecule, corre-

sponding, respectively, to these two products. After the soft rubber bonds are satisfied the addition of sulfur to a portion of the double bonds concerned in hard rubber formation gives rise to a third and unstable type of material, which we call intermediate or partially formed hard rubber.

4. Certain vulcanizing agents undergo only the soft rubber reaction, since they are incapable of adding to all the double bonds."

Garvey and Thompson<sup>7</sup> are of the opinion "that sulfur acts in at least two ways during vulcanization:

1. It causes vulcanization directly by sulfur addition.
2. It acts as a catalyst for a second reaction which also causes vulcanization. This second reaction is a reaction at the double bond of the hydrocarbon, which does not involve a change in its saturation."

### (c) Colloidal Theories

If we turn now to the colloidal theories of vulcanization we must consider first of all the critical survey of vulcanization which van Iterson<sup>8</sup> gave as far back as 1916. According to his second supposition, an "active" sulfur modification combines chemically with a part of the rubber to form a compound insoluble in the usual solvents, which subsequently combines "colloidally" with the remainder of the rubber to give an insoluble complex. A similar view has been independently expressed by Ostromislensky.<sup>9</sup>

It has been suggested<sup>10</sup> that vulcanized rubber should be considered as consisting of two phases, one soft, unchanged raw rubber, and the other the hard, tough compound of rubber hydrocarbon with sulfur in the ratio  $C_5H_8S$ . In later years H. P. Stevens has tried, in collaboration with W. H. Stevens,<sup>11</sup> to prove this opinion by a large amount of experimental work.

Twiss<sup>12</sup> also has expressed similar views, comparing the influence of  $C_5H_8S$  with the reinforcing properties of carbon black. Recently this same investigator<sup>13</sup> has again put forward experimental results to support this theory.

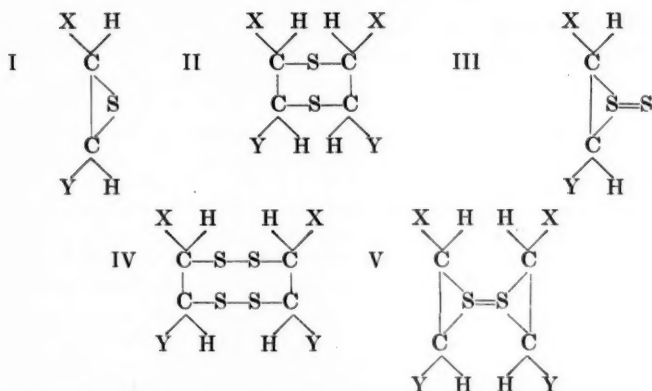
As mentioned above, it is not my intention to discuss the various theories at length, but I would like to spend my limited amount of time in indicating clearly my own standpoint in respect to the quintessence of vulcanization, and to confess myself as being a strong supporter of the chemical theory of vulcanization.

With regard to the "colloidal theory" of vulcanization, I must confess that I do not believe in it, however clever the experimental work that has been applied to prove this theory. In my opinion we can only look upon rubber as a mass of long chain rubber hydrocarbon molecules of varying length, and according to this view it is difficult to understand how during vulcanization a phase of hard rubber hydrocarbon-sulfur compound  $C_5H_8S$  can suddenly be developed, which would act as a kind of reinforcing material for the rest of the rubber hydrocarbon. I feel inclined to look upon this as an analogue of the theory of reinforcing compounding ingredients, but not as a picture of what really happens.

In what follows I will try to show that polymerization and chemical combination of rubber with sulfur are not mutually contradictory, but on the contrary are more closely related than is generally realized, and may easily be combined into one general chemical theory of vulcanization according to the views of Prins.

C. O. Weber did not consider hot vulcanization as a simple addition of sulfur to the double bond, as is obvious from the following quotation:<sup>14</sup>

"Respecting the configuration of any of the terms of this series ( $C_{100}H_{160}S$  to  $C_{100}H_{160}S_{20}$ , note by present writer) all is surmise, but the following possibilities exist:

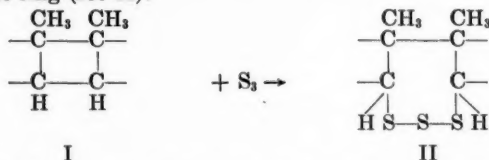


And on another page (i.e., p. 56) he wrote:

"At the present moment it still appears to me that the true vulcanizing effect consists not only in formation of an addition product, but also in a conjugation of india-rubber molecules in this manner (here follows formula II). And if this assumption be correct, it would follow that only divalent elements such as sulfur, but not monovalent elements such as Cl, or radicals such as HO, are capable of producing true vulcanization."

In the early part of 1914, Kirchhof,<sup>15</sup> on the basis of Harries' dimethyloctadiene formula for the rubber hydrocarbon, suggested that hot vulcanization should be considered as a transformation of the loosely polymerized hydrocarbon into a stable condensed system by the formation of tetramethylene rings (see I below).

Owing to the reactivity of this ring sulfur as thiosulfur (thioozone) would combine with the ring (see II).



The addition of  $S_3$  seems very unlikely, but the tetramethylene ring is an element which deserves consideration, even more than 20 years later.

I just want to quote one sentence which shows that Kirchhof, in 1914, saw vulcanization in exactly the same way as Hauser, Whitby, and others see it today. He wrote: "In diesem Zustande wirkt nun der gleichfalls reaktionsfähiger gewordene Schwefel kondensierend auf die Oktadienringe ein. Gleichzeitig findet Bindung eines Teiles des Schwefels statt. Letztere ist aber eher als eine notwendige Begleiterscheinung, als die eigentliche Ursache des Zustandes 'vulkanisiert' aufzufassen. Als diese kommt vielmehr die kondensierende (Katalytische) Wirkung in Betracht."\*

In 1920 Kirchhof considerably changed his views on vulcanization; he then suggested that the first stage of vulcanization is a sulfur bridge between two hydrocarbon molecules, and that only at higher temperatures and with higher sulfur concentrations does addition of sulfur at the double bond occur, leading to the ebonite stage of vulcanization.

\* In this state sulfur, having become reactive, has a condensing action on the octadiene ring. Binding of sulfur occurs, but this is to be considered more as an unavoidable side reaction than as the cause of the vulcanized state.



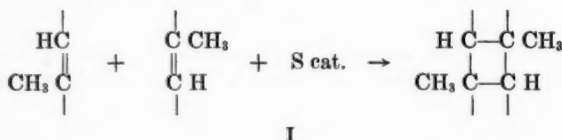
In 1918, Prins<sup>16</sup> put forward a general theory of the condensation of unsaturated hydrocarbons under catalytic influence, which he extended to the theory of vulcanization, and which has not been given the attention which it deserves. Prins had given already in 1911 a theory of the action of a catalyst on the basis of mutual activation. The catalyst activates the substance (s) going into reaction but on the other hand the catalyst is also activated. Under these circumstances a reaction between both may occur.

It is often observed that unsaturated substances, which react with O<sub>2</sub>, halogens, etc., take up considerably less of this substance than would be expected according to a simple addition reaction. According to Prins' theory this is quite comprehensible, because the activated unsaturated hydrocarbon will react with itself (polymerization), and also simultaneously with the other substance (condensation).

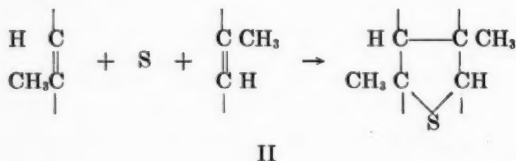
Prins has considered hot vulcanization with sulfur from this standpoint, and has given the following scheme. The sulfur, which may have been brought by vulcanization accelerators into a more active state, also brings the rubber hydrocarbon into a reactive state. Apart from the polymerization of the rubber hydrocarbon by the sulfur (as true catalyst), there can also take place reactions between hydrocarbon and sulfur in two different ways.

The reactions which, according to this theory, can be expected are the following:

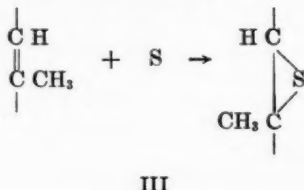
1. Polymerization.



2. Condensation of two molecules of rubber hydrocarbon with simultaneous reaction with sulfur.



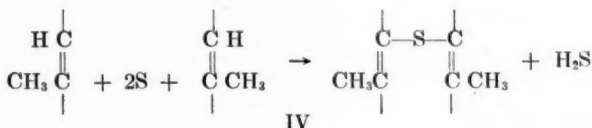
3. Simple addition of sulfur to the double bond.



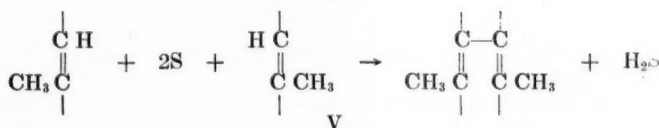
The advantage of this scheme of Prins lies in the fact that polymerization and sulfur binding are no longer opposite and alternative possibilities, but will occur simultaneously. This seems in full harmony with the facts of vulcanization, in which a certain amount of sulfur is always bound and cannot be removed by extraction.

With these three reactions, however, the possibilities are not exhausted. When sulfur reacts with rubber hydrocarbon there are still two other possibilities, which we may express in formulas IV and V.

4. Substitution of hydrogen with evolution of  $\text{H}_2\text{S}$ .



5. Dehydrogenation and polymerization.



These possibilities have already been mentioned in the literature.

In 1915, Ostromislensky<sup>17</sup> wrote: "When heated with unsaturated hydrocarbons, sulfur produces a two-fold effect; it combines at the double bond with formation of thiozonides (Erdmann), or it oxidizes the ethylene grouping, removing hydrogen in the form of hydrogen sulfide, a new ethylenic derivative or a new compound containing sulfur being thus formed."

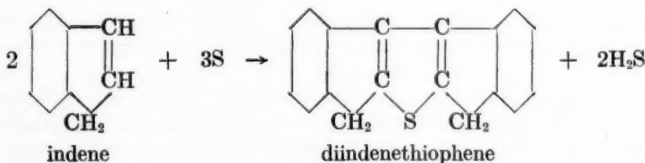
Little attention has been paid in the last twenty years to this useful suggestion probably owing to the fact that C. O. Weber, (*loc. cit.*) originally stated that vulcanization had to be considered as an addition.

We see from formulas I-V that the theory of Prins explains the combined possibilities of polymerization and condensation with S very well, and that apart from the direct S-binding at the double bond, the various possibilities all point to the formation of bridges with or without sulfur between the various  $(\text{C}_6\text{H}_5)_n$  molecules.

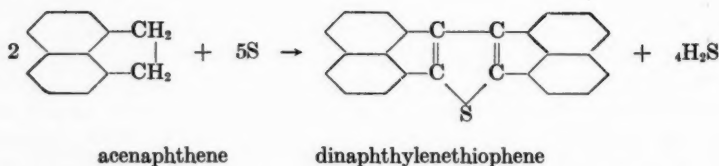
If the theory of Prins is correct, it should be possible to trace some analogue with respect to the behavior of sulfur towards other unsaturated hydrocarbons. If one considers the literature, it becomes obvious that this chapter of organic chemistry is very badly neglected, only a very few examples of such reactions being available.

Here follow a few reactions of aromatic hydrocarbons with sulfur, which were found in the older literature.

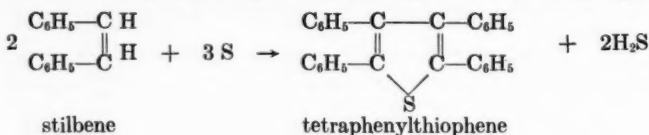
Friedmann<sup>18</sup> studied the reaction of indene with sulfur giving at  $185^\circ \text{C}$ . diindenethiophene.



Dziewonski<sup>19</sup> studied the reaction of acenaphthene with sulfur, which gives at  $205^\circ \text{C}$ . dinaphthylenethiophene, according to the following equation:

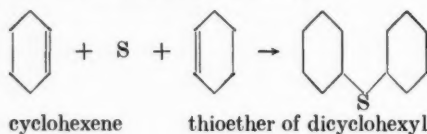


Baumann and Fromm<sup>20</sup> have studied the reaction of stilbene with sulfur, which gives at 200° C. tetraphenylthiophene according to the following equation:

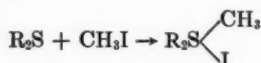


These three reactions give an example of dehydrogenation with the formation of  $\text{H}_2\text{S}$  according to formula IV.

Recently, Meyer and Hohenemser<sup>21</sup> have studied the reaction of cyclohexene with sulfur at 140–150° C. yielding, apart from a mercaptan, the thioether of dicyclohexyl, according to the following equation:



These investigators also gave a reaction for the determination of the C-S-C group, *viz.*, with methyl iodide



They applied this reaction also to the determination of the C-S-C group in vulcanized rubber, which according to the authors does not give any difficulty. This is a very important point, and the reaction should certainly be applied to a great number of vulcanization problems. While considering the dehydrogenation reactions (formulas IV and V) we may also refer to the work of Ruzicka,<sup>22</sup> who used the dehydrogenation reaction with sulfur for the elucidation of the constitution of sesquiterpenes. It should be mentioned that Diels and his co-workers have also used selenium for the dehydrogenation of organic compounds, and it seems more than accidental that this element is also able to produce vulcanization under certain conditions.

If vulcanization occurs partly according to formulas (II) and (IV), we must expect a certain amount of  $\text{H}_2\text{S}$ . For this reason the question should be raised: Is there any experimental evidence that hydrogen sulfide is formed during vulcanization?

Wolesensky<sup>23</sup> has described various experiments showing the evolution of  $\text{H}_2\text{S}$  from ebonite as well as from soft vulcanized rubber, and later Cummings<sup>24</sup> studied the influence of temperature on the evolution of hydrogen sulfide.

In the Netherlands Government Rubber Institute at Delft, Dekker has carried out an investigation to verify whether hydrogen sulfide was evolved during vulcanization, and under what conditions.

A rubber-sulfur mixture was put in a porcelain dish in a glass tube, which by means of an air bath was kept at the desired temperature. A slow current of nitrogen was sent through the tube, and any hydrogen sulfide evolved was absorbed in a vessel containing sodium hydroxide, oxidized with bromine, and determined as barium sulfate. These experiments have been carried out with various rubber-sulfur mixings, and certain amounts of hydrogen sulfide detected. As there was a possibility that the hydrogen sulfide originated from the action of the sulfur on the acetone extract of the rubber, further experiments have been carried out with mixings of acetone-extracted rubber, 92.5 parts, and sulfur, 7.5 parts. Table I gives a few of the figures obtained with this mixing at various temperatures.

TABLE I  
PERCENTAGE OF SULFUR LIBERATED AS HYDROGEN SULFIDE DURING VULCANIZATION

Time of Cure	Temperature	
	130° C.	150° C.
0-2 hours	0.06%	0.27%
2-4 hours	0.17%	0.12%
4-6 hours	0.19%	0.06%
	0.42%	0.45%

It is doubtful if all the hydrogen sulfide developed is determined quantitatively, but from Dekker's experiments we may certainly conclude that during vulcanization of soft vulcanized rubber an appreciable amount of hydrogen sulfide is developed, which must find its origin in a dehydrogenation of rubber by sulfur. This gives a certain amount of evidence to support reactions IV and V. It is not clear what is the role of this hydrogen sulfide developed under normal vulcanization conditions. There is, perhaps, a possibility of oxidation to sulfur by oxygen present in the rubber; there might also be a reaction of hydrogen sulfide with the double bonds. It is a remarkable fact that so little is known of the reaction of hydrogen sulfide with unsaturated hydrocarbons.

The theory as proposed by Prins and extended somewhat by the present writer seems to explain the facts of vulcanization in a reasonable way. Without going into details we may refer to the following points:

1. On the basis of a sulfur addition at the double bond, *e. g.*, as given in the theory of Boggs and Blake, it would be impossible to understand why the properties of the long chain rubber molecules were changed in such a remarkable degree by such a small amount of sulfur. It is well known that Bruni<sup>25</sup> stated that even such a small amount as 0.15 per cent of combined sulfur caused the phenomenon of vulcanization. This can be understood on the basis of the present theory. Firstly, a few sulfur bridges here and there will bind together a large number of long chain rubber molecules, and, moreover, apart from sulfur binding, polymerization comes in so that bridges without sulfur may do the rest.

2. On this basis it is understandable why soft vulcanized rubber no longer dissolves in organic solvents. Large molecules extending in three dimensions have been formed.

3. The change in mechanical properties can be understood. By mastication the long chain molecules are broken down, probably under the influence of the oxygen present, or perhaps peroxides. The rubber becomes more plastic. By vulcanization bridges are formed, with the result that plasticity quickly diminishes and the elasticity quickly increases.

4. As is well known from experiments of Nauck and Lange,<sup>26</sup> and also from those of Boiry,<sup>27</sup> it is possible, in the early stages of soft rubber vulcanization, to

extract by various solvents a certain amount of "vulcanized rubber." This seems to point to a certain lack of homogeneity, which is understandable, because according to the above theory a variety of reactions play a part in the vulcanization process.

5. In the case of ebonite formation, addition of sulfur at the double bonds will occur, and at the same time a certain amount of dehydrogenation with formation of hydrogen sulfide.

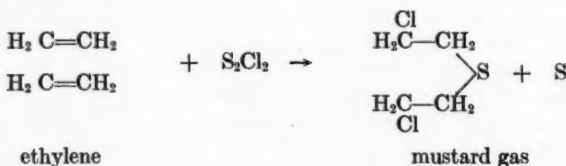
As was shown by Stevens and Stevens,<sup>28</sup> this substitution explains the fact that the amount of combined sulfur may rise above 32 per cent. In this connection it may be pointed out that Midgley, Henne, and Shepard<sup>29</sup> have given a formula for the structure of ebonite, which agrees fairly well with the suggestions made above.

If we now consider other vulcanization processes, we shall see from the following that the theory of "bridge building" between the long chain rubber hydrocarbon molecules is also applicable to the other vulcanization processes, among which we will only draw attention to cold vulcanization and vulcanization with benzoyl peroxide.

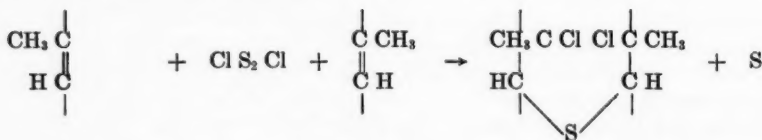
#### Cold Vulcanization

Weber<sup>30</sup> had already pointed out that the reaction of sulfur chloride with rubber, the so-called cold vulcanization process, was an addition process, and would be similar to the reaction of  $S_2Cl_2$  with other unsaturated hydrocarbons. He referred to Guthrie,<sup>31</sup> who investigated the reaction of  $S_2Cl_2$  on ethylene and amylene, and obtained the compounds  $(C_2H_4)_2 S_2Cl_2$  and  $(C_5H_{10})_2 S_2Cl_2$ .

Similar views were expressed by Meyer and Mark<sup>32</sup> a few years ago. The reaction of ethylene with  $S_2Cl_2$  gives  $\beta\beta'$ -dichlorodiethyl sulfide (mustard gas), according to the equation:



By analogy with this reaction the cold vulcanization of rubber may be represented by the following reaction:



As is obvious from this formula, there is also in the case of cold vulcanization a sulfur-binding between two carbon atoms  $[-C-S-C-]$ .

Recently, Meyer and Hohenemser<sup>33</sup> have proved this supposition experimentally by determining the amount of sulfur bound as  $C-S-C$  by their methyl iodide method.

Considering also the fact that sulfur in the nascent state is developed during this reaction, it is evident that this sulfur will act as a catalyst for the polymerization reaction of the rubber hydrocarbon. These considerations make it appear



probable that during cold vulcanization of rubber similar reactions occur to those taking place during hot vulcanization.

Cold vulcanization also is characterized by "bridge-like" condensations of the hydrocarbon, with or without sulfur in between.

#### Vulcanization with Benzoyl Peroxide

The vulcanization of rubber with benzoyl peroxide, discovered by Ostromislensky<sup>34</sup> in 1915, has been the subject of much speculation with respect to the causes of this reaction. The most probable suggestion was that of Twiss,<sup>35</sup> who supposed that the benzoyl peroxide fulfilled the role of a catalyst of polymerization, and that the vulcanization was principally a polymerization process.

This vulcanization process has been further investigated in the Netherlands Government Rubber Institute.<sup>36</sup> If we vulcanize a mix of F. L. rubber, 90 parts, and 10 parts of benzoyl peroxide at 147° C., vulcanization proceeds very quickly and is already finished in about 10 minutes, as is obvious from the figures in Table II. The vulcanized rubber was soon covered with a bloom, which was easily identified as crystals of benzoic acid. It therefore seemed of importance to determine the amount of benzoic acid in the vulcanized rubber. Table II gives the figures which were obtained with a vulcanized mixing of the composition already stated.

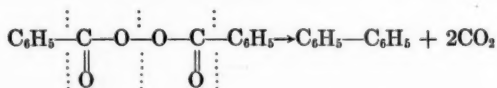
TABLE II  
VULCANIZATION WITH BENZOYL PEROXIDE  
MIX: RUBBER 90 PARTS, B. P. 10 PARTS

	Time of Cure at 147° C.		
	10	30	60 Min.
Acetone extract	6.8%	6.9%	7.1%
Benzoic acid in acetone extract	3.7%	3.8%	3.9%
Alcoholic potash extract	3.1%	2.7%	2.8%
Benzoic acid in alcoholic potash extract	2.2%	1.9%	2.0%
Benzoic acid (total)	5.9%	5.7%	5.9%

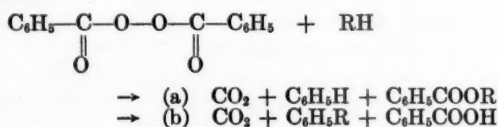
Similar figures are obtained when the vulcanization is carried out at 120° C. As is obvious from these figures, more than half of the benzoyl peroxide is recovered as benzoic acid.

Through the researches of Gelissen,<sup>37</sup> Hermans,<sup>38</sup> and Reynhardt,<sup>39</sup> we know that the diacylperoxides, among which is benzoyl peroxide, may decompose according to the following reaction schemes:

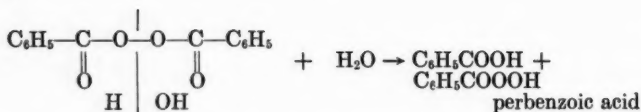
1. Pyrogenic decomposition with formation of 2 molecules of CO<sub>2</sub> and diphenyl.



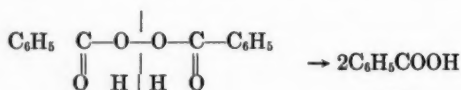
2. Decomposition, according to the so-called R-H scheme, with evolution of one molecule CO<sub>2</sub>



3. Decomposition by bases, alcohols, etc., where the diacyl peroxide reacts as a mixed acid anhydride of peracid and acid.



4. Through the addition of 2H a symmetrical breakdown into two molecules of benzoic acid.

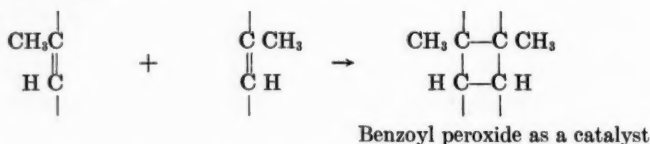


This process occurs in reactions with compounds which can yield hydrogen, or in other words, are able to undergo dehydrogenation.

Reactions 1 and 2 are excluded with rubber, because during vulcanization no trace of carbon dioxide is developed. Reaction scheme 3 is also very improbable, as no base or alcohol is present in rubber. So the only decomposition scheme which seems likely to occur during vulcanization is scheme 4, where the rubber hydrocarbon undergoes dehydrogenation, which will result in the formation of benzoic acid. This is in accordance with the fact that a considerable quantity of benzoic acid is found after vulcanization. It is only fair also to mention the view of Pummerer and Bock,<sup>40</sup> who were both of the opinion that a benzoxylation of rubber occurs, part of the benzoic acid being bound to the rubber. It is probably this part that is recovered as benzoic acid when the acetone-extracted rubber is treated with alcoholic potash.

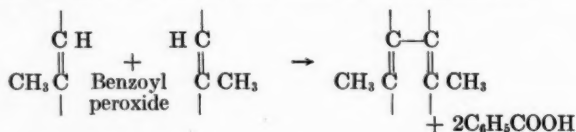
If we now consider what may happen during vulcanization with benzoyl peroxide, we come to the following reactions:

1. Polymerization reaction, under the influence of benzoyl peroxide as a catalyst. It is a well-known fact that peroxides in many cases act as catalysts to polymerization reactions<sup>41</sup>



2. Benzoxylation according to Pummerer and Bock.

3. Dehydrogenation and subsequent condensation as follows:



As is obvious from the formula, we get in cases 1 and 3 once again binding of the long chain rubber hydrocarbon molecules, which accounts for the changes in properties that occur during vulcanization.

From the foregoing it seems evident that the various vulcanization processes may be considered from the same point of view, and that the same theory holds true in these different cases.

In the opinion of the writer, the quintessence of vulcanization lies in "bridge-building" between the long chain rubber hydrocarbon molecules.

By these "bridges" large complexes are built up, which explain the change in properties during vulcanization.

This "bridge-building" may be a simple polymerization, or sulfur bridges of the formula  $C-S-C$ , or dehydrogenation under the influence of sulfur with subsequent condensation. The theory of Prins (1918) explains very well how polymerization and chemical combination of rubber with sulfur occur simultaneously during vulcanization, an old controversy being settled in this way.

### References

- <sup>1</sup> C. O. Weber, "The Chemistry of India-Rubber," London, 1902.
- <sup>2</sup> Wo. Ostwald, *Z. Kolloidchemie*, **6**, 136 (1910).
- <sup>3</sup> Hauser, *Trans. Inst. Rubber Ind.*, **2**, 243, 300 (1926).
- <sup>4</sup> Schidrowitz, *India-Rubber J.*, **74**, 802 (1927).
- <sup>5</sup> Whitby, *Trans. Inst. Rubber Ind.*, **6**, 61 (1930).
- <sup>6</sup> Boggs and Blake, *Ind. Eng. Chem.*, **22**, 748 (1930).
- <sup>7</sup> Garvey and Thompson, *Ibid.*, **25**, 1292 (1933).
- <sup>8</sup> van Iterson, Communications of the Netherlands Government Rubber Institute, Part VII, p. 239 (1918), also *Kolloidchem. Beihefte*, **12**, 252 (1920).
- <sup>9</sup> I. Ostromislensky, *J. Russ. Phys.-Chem. Soc.*, 1453, 1462, 1467 (1915); translated *India-Rubber J.*, **52**, 467, 470 (1916).
- <sup>10</sup> Stevens, "Fourth Report on Colloid Chemistry," p. 366 (1922).
- <sup>11</sup> Hübener, *Chem.-Ztg.*, **33**, 144, 157 (1909); Porritt and Wheatley, "Rubber Industry," **1914**, p. 199; H. P. Stevens and W. H. Stevens, *J. Soc. Chem. Ind.*, **47**, 37T (1928); **48**, 55T, 60T (1929); **51**, 44T (1932).
- <sup>12</sup> Twiss, *J. Soc. Chem. Ind.*, **44**, 106T (1925).
- <sup>13</sup> Twiss, *Trans. Inst. Rubber Ind.*, **9**, 275 (1934).
- <sup>14</sup> C. O. Weber, *loc. cit.*, p. 92.
- <sup>15</sup> Kirchhof, *Kolloid Z.*, **14**, 35 (1914).
- <sup>16</sup> *Chemisch Weekblad*, **16**, 64 (1918).
- <sup>17</sup> Ostromislensky, *loc. cit.*
- <sup>18</sup> Friedmann, *Ber.*, **49**, 50, 1551 (1915).
- <sup>19</sup> Dziewonski, *Ber.*, **36**, 965, 3768 (1903).
- <sup>20</sup> Baumann and Fromm, *Ber.*, **24**, 1456 (1891); **28**, 893 (1895).
- <sup>21</sup> Meyer and Hohenemser, *Helv. Chim. Acta*, **18**, 1061 (1935).
- <sup>22</sup> Ruzicka, "Über Konstitution und Zusammenhänge in der Sesquiterpenreihe," *Fortschritte Chemie, Physik und Physikalische Chemie*, **19**, No. 5 (1928).
- <sup>23</sup> Wolesensky, *J. Research Bur. Standards*, **4**, 501 (1930).
- <sup>24</sup> Cummings, *Ibid.*, **9**, 163 (1932).
- <sup>25</sup> Bruni, *Rev. Gén. Caoutchouc*, **8**, No. 75, 19; *RUBBER CHEM. TECH.*, **5**, 295 (1932).
- <sup>26</sup> Nauck and Lange, *Kolloid Z.*, **34**, 297 (1924).
- <sup>27</sup> Boiry, *India-Rubber J.*, **68**, 651, 687, 727, 771, 807 (1924).
- <sup>28</sup> H. P. Stevens and W. H. Stevens, *J. Soc. Chem. Ind.*, **48**, 55T (1929). See also Fisher and Schubert, *Ind. Eng. Chem.*, **28**, 209 (1936).
- <sup>29</sup> Midgley, Henne, and Shepard, *J. Am. Chem. Soc.*, **56**, 1326 (1934).
- <sup>30</sup> C. O. Weber, *loc. cit.*, p. 97.
- <sup>31</sup> Guthrie, *Ann.*, **113**, 270 (1860).
- <sup>32</sup> Meyer and Mark, *Ber.*, **61**, 1939 (1928).
- <sup>33</sup> Meyer and Hohenemser, *Helv. Chem. Acta*, **18**, 1061 (1935).
- <sup>34</sup> Ostromislensky, *J. Russian Phys.-Chem. Soc.*, **47**, 1453, 1462, 1467 (1915); translated *India-Rubber J.*, **52**, 467 (1916).
- <sup>35</sup> Twiss, *Trans. Inst. Rubber Ind.*, **5**, 184 (1929); **6**, 40 (1930).
- <sup>36</sup> van Rossem, Dekker and Prawirodipoero, *Kautschuk*, **7**, 202, 219 (1931).
- <sup>37</sup> Gelissen, "Over Diacylperoxyden, Hunne Constitutie en Hunne Beteekenis voor de Chemische Synthese" (Dissertation, Delft), 1926.
- <sup>38</sup> Gelissen and Hermans, *Ber.*, **58**, 285, 476, 480, 764, 765, 770, 984, 2396 (1925); **59**, 63 (1926).
- <sup>39</sup> Reynhardt, "Studies in de chemie der Peroxyden," (Dissertation, Delft), 1926.
- <sup>40</sup> Pummerer and Bock, Discussion on paper by van Rossem, *et al.*, *Kautschuk*, **7**, 224 (1931).
- <sup>41</sup> See, e. g., Riechie, "Die Bedeutung der organischen Peroxyde für die chemische Wissenschaft und Technik" (Sammlung Chemischer und Chemisch-technischer Vorträge, Neue Folge, Heft 34), 1936, p. 64.

# The Rheology of Raw Rubber

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## Introduction

The scientific measurement of the rheological properties of raw or unvulcanized rubber is a problem that has required new methods in rheological laboratory technique. Hot, moderately milled, or masticated raw rubber exhibits to a very marked degree each of the three properties of elasticity, plasticity, and thixotropy. It is highly elastic (not perfectly elastic), in that if deformed and released quickly it can take a large deformation and still return to its initial form. It is highly plastic, in that under proper conditions it can be deformed to any given extent permanently and without rupture. It is highly thixotropic, in that its viscosity or stiffness is very considerably decreased by brief mechanical working or mastication, and the lost viscosity is largely regained again when the mastication ceases. Obviously such a wide and varied range in rheological properties cannot be measured in either of the two types of rheological instruments, the compression and the extrusion plastometers, commonly used for raw rubber. There is no way in either instrument to determine or correct for thixotropy; and the viscosity can only be calculated with considerable uncertainty and difficulty. For example, thixotropy has not been considered in either of the already very complicated analyses of parallel plate plastometry by Peek<sup>1</sup> and by Scott.<sup>2</sup> Peek and Erickson<sup>3</sup> have attempted to analyze the effects of thixotropy and elasticity in capillary tube viscometry without obtaining a complete or generally useful solution. However useful the compression and extrusion plastometers may be in factory control work, they are inadequate as scientific research instruments.

The rotating cylinder viscometer seems to be the only type of instrument that meets the requirements of the problem considered. It allows an unlimited deformation of the test material, the previous deformation history can be controlled at will, and the subsequent elastic recovery can be measured if desired. There are two serious deficiencies of the conventional cylindrical viscometer, as applied to raw rubber, in that, first, the rubber, being semi-solid, would be likely to slip on the moving surfaces; secondly, if the rubber did not slip but sheared as it should, it would soon roll and climb out of the viscometer against the force of gravity. These deficiencies can be corrected, first, by fluting or otherwise roughening the cylindrical surfaces so that they grip the rubber and prevent slipping; secondly, by adding means for compressing and holding the rubber in place.

The combined use of these two devices in a factory control instrument, the rotating disc plastometer, has already been described; and a rotating cylinder viscometer with similar features was referred to in the same article.<sup>4</sup> The cylindrical viscometer there referred to was used in the experimental researches described below. Since this instrument is so different in several respects from the conventional cylindrical viscometers and, furthermore, is designed to facilitate the measurement of thixotropy and elastic recovery as well as viscosity, it seems appropriate to give it a new name and call it a *rubber rheometer*.

## Description of the Rheometer

The details of the instrument are shown in Figs. 1 and 2. The outer, stationary cylinder, or stator, is split into two halves, 1 and 2, hinged on the support rod 3.

When the two halves are open, rubber samples can be inserted or removed. In the closed position the two halves are locked to the support rod 4 by the bolt 5 and lock nut 6.

The inner cylinder, or rotor, 7, is mounted on the hollow shaft 8, which turns in the ball-bearings 9, 10, and 11. The surfaces of stator and rotor are each fluted longitudinally with a series of 60° V-grooves, about 90 to the inch, cut full depth, to form a series of sharp ridges.

The necessary confining pressure on the rubber sample between rotor and stator is produced by the weights 12 and 13, operating on the pressure rings 14 and 15,

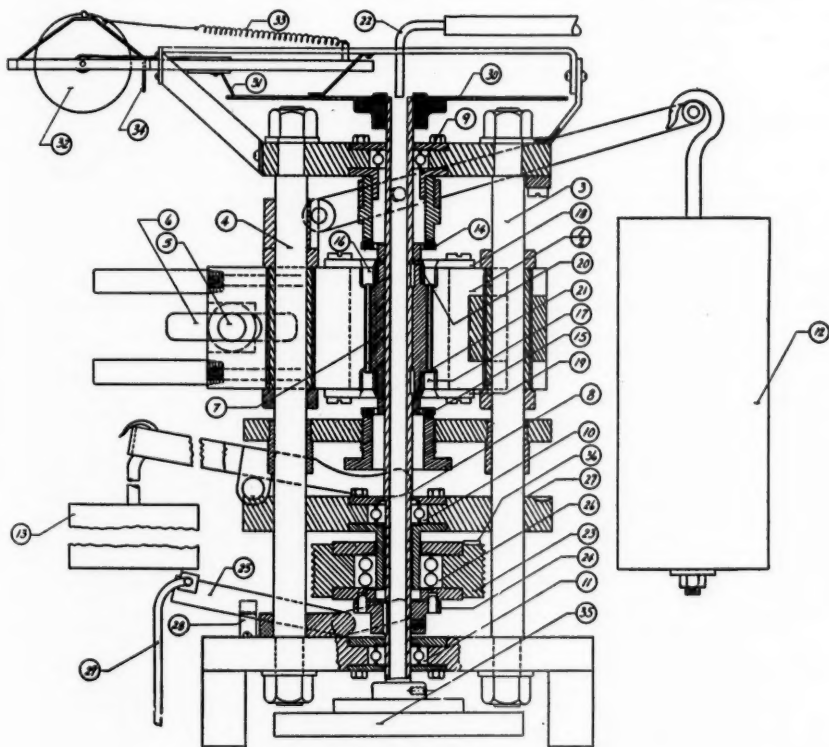


Figure 1—The Rubber Rheometer

respectively. These rings, faced with soft vulcanized rubber pads, fit into the circular channels 16 and 17, respectively, cut into the rotor and stator above and below the fluted gripping surfaces. These channels serve as rubber reservoirs, from which reserve rubber is forced into the narrow space between the fluted surfaces as trapped air in that region works out or as rubber leaks out between the two halves of the stator. Four semi-circular, beveled guide plates, such as 18 and 19, keep the rubber pressure pads from cutting or tearing on the edges of the reservoir channels. After a new sample of rubber has been inserted, the beveled plates are removed, the excess rubber above and below the stator blocks is cut away, and the beveled plates replaced again before the pressure pads are forced into the reservoir channels.



The inner surfaces of these channels are formed by the collars 20 and 21, which rotate freely on the rotor shaft.

The rotor is heated by oil, which is pumped from a controlled-temperature oil bath through the tube 22, and circulates through the hollow shaft by gravity. The stator is heated by oil from the same bath, pumped through cavities in the stator blocks not shown in the drawings.

The driving torque operating on the rotor is obtained by driving weights con-

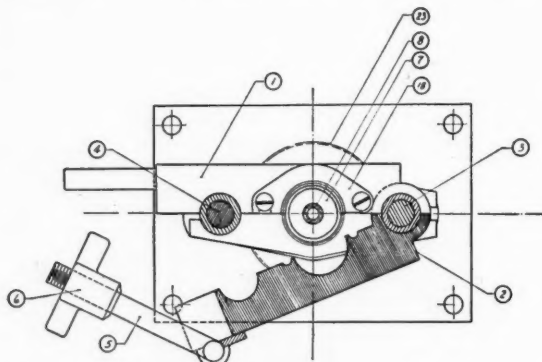


Figure 2—The Rubber Rheometer

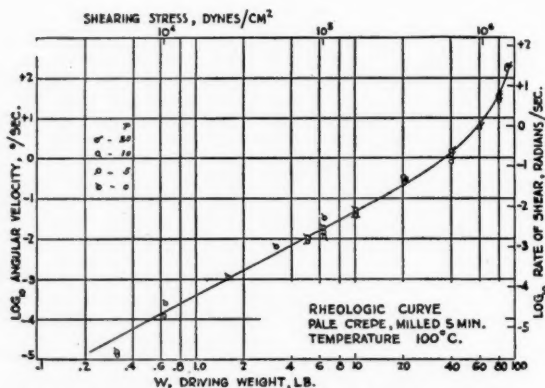


Figure 3—Typical Rheologic Curve of Rubber

needed by a small steel cable to the sheave 23. The sheave can be connected to or disconnected from the rotor shaft by means of the clutch 24, operated by the clutch handle 25. When the clutch is released, the sheave is entirely disconnected from the shaft 8, since its ball-bearing support, 26, is mounted not on the shaft, but on the plate 27. The clutch handle operates by raising the sheave to clear the pins in the clutch when the handle is down. The spring catch, 28, shown only in outline, serves to hold the handle up; but the handle can be forced down in spite of this spring, thus releasing the clutch, when a weight is dropped in a stirrup, 29, supported on the clutch handle and extending below the base of the rheometer.

The aluminum disc, 30, mounted on the upper end of the rotor shaft, carries a

Central Scientific Company sensitive waxed chart, graduated in degrees. Slow or moderate rates of rotation are measured visually, with the aid of a stopwatch. At high rates of rotation, a spark record is produced on the sensitive chart by means of a Cenco Spark timer, set at a frequency of 5 sparks per second.

The stylus, 31, can be pulled radially across the face of the chart by a thread attached to a small drum mounted with a friction fitted on the shaft of the fly-wheel, 32. This fly-wheel can be suddenly set into rotation by the spring 33, when the trigger, 34, is pulled. The trigger is pulled by a string attached to the same weight that releases the clutch. It is thus possible to start the stylus moving radially across the chart just before the clutch is released and thus obtain an autographic record of elastic recovery of the sample immediately after the shearing stress is released.

The stylus serves also as the sparking point in making spark records of high rotational velocities. In this case the stylus is given a slow radial motion by means of a suitably connected, weighted string wound once around the rotor shaft. The fly-wheel, 35, is added to the lower end of the rotor shaft to increase the moment of inertia of the rotor system.

Other accessories, not shown in the drawings, include electrical devices for dropping the clutch-releasing weight, either while the rotor is still moving or at a fixed time after the rotor has been stopped. The stopping device consists merely of a sheet of red fiber, with an electrical contact, inserted between the support rod and the small stopping nut, 36, on top of the sheave. Very slow rates of rotation of the rotor are sometimes measured with a micrometer gage with its foot resting against a small clamp temporarily attached to the edge of the aluminum disc. Mounted on the edge of the table supporting the rheometer there is a windlass for lifting the driving weights. The clutch handle has attached to it a spring which starts a stopwatch when the clutch is released.

#### *Constants of the Apparatus*

Length of rotor and stator	5.08 cm. (2 in.)
Radius of rotor (to top of ridges)	1.70 cm.
Radius of stator (to top of ridges)	1.90 cm.
Effective radius of sheave	5.05 cm.
Moment of inertia of rotor system	$6.03 \times 10^4$ g.-sq. cm.
Mean shearing stress	$\sigma = 2.11 \times 10^4 W$ dynes per sq. cm.
	$W =$ driving weight in lb.
Mean rate of shear	$\frac{d\alpha}{dt} = 0.162\omega$ radians per sec.
Speed of tracer	$\omega =$ rotor velocity in degrees per sec.
	$= 20$ cm. per sec.
Pressure on the rubber	$= 4.4 \times P$ (lb. per sq. in.)
	$= 0.275 \times P$ (kg. per sq. cm.)

where  $P$  = the pressure weight in lb.

The above expressions for  $\sigma$  and  $d\alpha/dt$  are calculated by means of formulas previously published by the author.<sup>5</sup> To allow for end effects the clearance between rotor and stator was added to their actual length to obtain what was assumed to be their effective length.

*Discussion of the Apparatus.*—There are certain features of the rubber rheometer in its present form which could be improved upon. The rubber works in behind the collars 20 and 21; and these collars have to be moved up or down occasionally and cleaned out. They would give less trouble if they were designed with more free space inside between the collar and the shaft and with holes above, or below, so that the rubber that works in under the force of the pressure rings could also work out at the other end of the collar. The rubber facing on the pressure rings has to be renewed occasionally; and it could probably be satisfac-

torily replaced with metal faces fitting closely in the rubber reservoirs. The collars on the rotor, which were added after a solid rotor was found unsatisfactory, would probably prevent binding of the rotor by the metal pressure rings just as well as they prevent such effects with the rubber-faced pressure rings. The weights actuating the pressure rings should be augmented by screws to hold the rings firmly against the rubber; for it was found that sometimes with a large driving weight working on rather tough rubber, the rubber pushes against the pressure rings enough to force the pressure weights up a few thousandths of a centimeter. The resulting rate of rotation is certainly then too high; and a number of revolutions of the rotor with a lower weight are required before the rubber is compacted again and gives its former readings with the lower weight.

#### Experimental Results: Rheological Curves

The normal driving weight used in measuring the viscosity of raw rubber is from 9 to 45 kg. (20 to 100 lb.). Weights as high as 70 kg. (150 lb.) have been used and as low as 14 g. (0.3 lb.). The usual pressure weight used is 9 kg. (20 lb.), but with the lower driving weights it is customary to reduce or eliminate entirely the pressure weights, since there is a small but observable friction due to the pressure rings. There is friction also in the sheave, steel cable, and pulley, necessarily designed for heavy loads; for driving weights of 2 kg. (5 lb.) or less the clutch is released and the driving torque is applied by a cord wrapped around the fly-wheel and passing over a light pulley with conical bearings.

When the driving torque is applied to the rotor, the speed of rotation increases at first and then attains a practically constant value in one-eighth to one-quarter of a revolution under customary operating conditions. Under low torque, constant speed is attained within a smaller rotational angle, but more time is required. Under very high torques, less time is required, but more rotation; and in extreme cases constant speed may not be attained before the driving weight hits the floor, which occurs after two complete revolutions of the rotor. No detailed study of these thixotropic effects has yet been made, and the data reported in the present paper were all obtained after essentially constant angular velocity had been attained.

Figure 3 shows, on a logarithmic graph, the rheological curve at 100° C. for a sample of pale crepe given a moderate break down of 10 minutes on a laboratory mill. The different values of  $P$ , indicated by the various insignia as shown on the graph, are the pressure weights operating on the pressure rings. The straight part of the curve is represented by the equation

$$(d\alpha/dt) = 0.9 \times 10^{-12} \sigma^2$$

where  $d\alpha/dt$  is the rate of shear in radians per sec., or cm. per sec. per cm., and  $\sigma$  is the shearing stress in dynes per sq. cm. If we define the fluidity  $\varphi$ , and the coefficient of viscosity,  $\eta$ , as

$$1/\varphi = \eta = \sigma/(d\alpha/dt),$$

then

$$1/\varphi = \eta = 1.1 \times 10^{12}/\sigma = 1.05 \times 10^{-6}/\alpha^{1/2}.$$

The upward turn of the curve at the higher shearing stresses is found with all types of rubber so far examined. This feature is in general more marked the lower the temperature of the measurement and the less the break-down of the rubber.

Differences of this nature are seen in Fig. 4, which shows the rheological curves

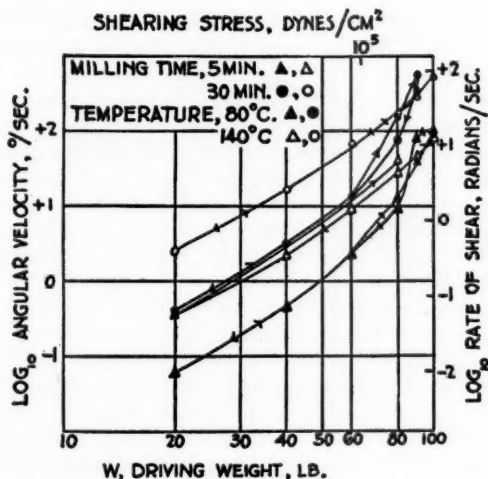


Figure 4—Rheologic Curves for Pale Crepe Rubber, Showing Effect of Breakdown and of Temperature

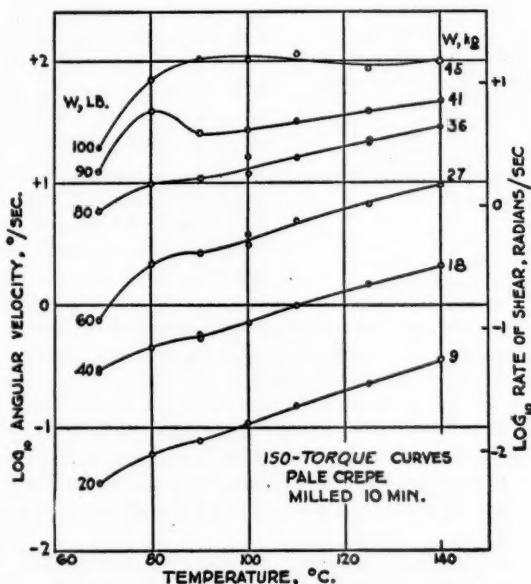


Figure 5—Iso-torque Curves, Showing Anomalous Temperature Effects

at 80° and 140° C. of pale crepe with a slight, 5 min., and a severe, 30 min., breakdown. At 40 kg. (90 lb.) driving weight the curve for the more masticated rubber lies above the other, showing that at this stress the "harder" rubber has the lower viscosity. The arrows, indicating the sequence of measurements, show a hysteresis between 25 and 40 kg. (60 and 90 lb.) load in the less milled sample. The remarkable feature about this hysteresis is that it indicates a negative thixotropy,

or a hardening of the material due to mechanical working. The cause of this phenomenon is at present very uncertain. A possible explanation is that the structure of the rubber, which is inhomogeneous itself and contains foreign particles of protein and other materials, is changed at high rates of shear and a phenomenon similar to work-hardening of metals is produced.

In Fig. 5 are shown the iso-torque curves for rate of shear plotted against temperature for a sample of moderately milled pale crepe. The curves show a point of inflection and in some cases a maximum in the region of 80° to 90° C. This effect is rather surprising, but has been found in other cases, though only with slightly or moderately milled rubber. Thoroughly milled rubber does not show it.

We can explain this phenomenon if we consider that the viscosity of rubber depends upon two properties, first, the forces of adhesion between the stable structural units, which determine how readily they yield and part or slip past each other under the shearing stress; and second, the speed with which the forces of adhesion are reestablished in the new or continuously changing arrangement of the structural units. It is well known to all rubber workers that two pieces of warm, raw

rubber, when forced into contact, do not stick together nearly as firmly at first as after being left in contact for a few minutes or hours. It is not unreasonable to suppose that likewise, in a sample of rubber subjected to shear, the adhesive forces require finite time to attain their full strength between the relatively moving structural units in the material. If this is the case, then in order to explain Fig. 5 we need only to assume the proper relationships between temperature and the two properties of ultimate adhesive force, and the rate at which the ultimate adhesive force is reestablished. Thus, we may assume that the ultimate force con-

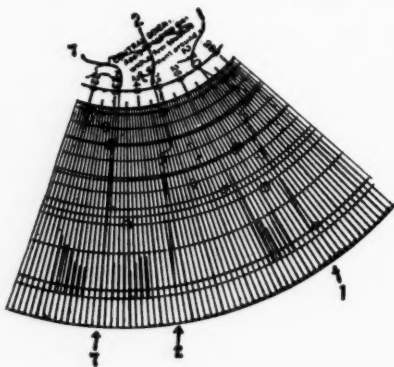


Figure 6—Elastic Recovery Records

tinuously decreases with temperature, and that the rate of reestablishment continuously increases with temperature; but that at about 80° to 90° C. the rate of reestablishment increases relatively faster than the ultimate force decreases. The net result is then, according to this hypothesis, that the *average* adhesive force actually maintained between the moving structural units of the rubber may increase with temperature in the indicated region, or at least not decrease as rapidly as on either side of this region. What actually happens would be expected to depend upon the rate of shear and perhaps also the shearing stress, as is shown by the experimental data.

The question has been raised whether the effects shown in Fig. 5 might result from a temperature increase in the rubber due to the viscous dissipation of energy during shearing. The question can be answered definitely in the negative. The temperature increase at the center of the sample during continuous shearing can be calculated from the thermal conductivity of rubber, the surfaces being assumed at the temperature of the rheometer. The result is:

$$\Delta T (^{\circ}\text{C.}) = 5.8 \times 10^{-4} W \omega$$

where  $W$  is the driving weight in pounds and  $\omega$  the angular velocity of the rotor in degrees per second. According to this formula the temperature rise would be



less than  $2^{\circ}\text{C}$ . in the worst case, which is quite inadequate to account for the anomalies observed.

### Elastic Recovery

Elastic recovery in the rubber rheometer is measured by observing the reverse rotation of the rotor after the driving torque is removed. As was indicated in the

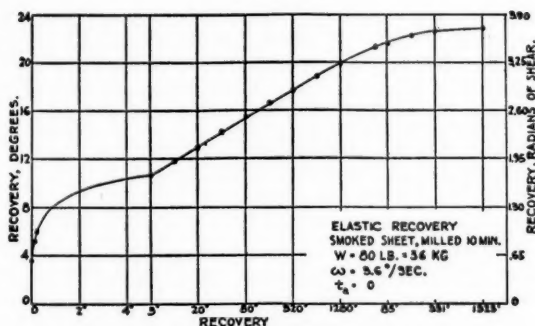


Figure 7—Typical Elastic Recovery Curve

description of the instrument, reverse rotation can be allowed either immediately on removal of the driving torque or after the rotor has been held stationary for a given time interval. This time interval between stoppage and permitting reverse rotation is called the *annealing time* and is denoted by  $t_a$ .

Some typical autographic records of elastic recovery are shown in Fig. 6, and

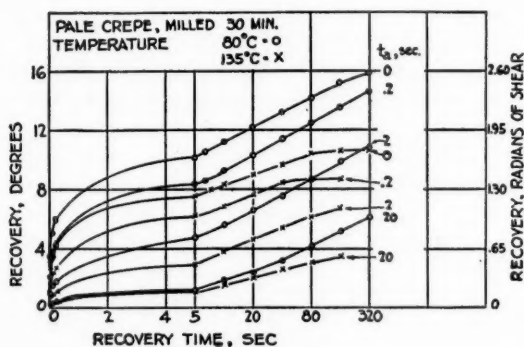


Figure 8—Elastic Recovery Curves, Showing Effects of Annealing and of Temperature

the conditions preceding the recovery records are indicated in the table below the figure.

The recovery begins with the wavy portion of the curve. The waves result from the oscillations of the rotor, quickly damped, due to the elastic stress in the rubber at the moment of release.

The autographic record covers the first 0.2 second of recovery. After that the record is obtained by manual operation of the stylus, which produces the series

of short radial lines near the periphery of the chart. (The series of points in the small circles are spark records, used for measuring the speed of rotation at high speeds.) The first manual record is made at 5 seconds after recovery begins. During this first 5 seconds the pressure rings are removed so as to eliminate friction as far as possible during recovery.

A complete elastic recovery curve is shown in Fig. 7. The time scale is linear up to 5 seconds, and logarithmic thereafter. In the right-hand recovery scale the unit of one radian is equivalent to one cm. shear per cm. thickness. The driving weight prior to recovery was 36 kg. (80 lb.), and the angular velocity of the rotor was  $3.6^\circ$  per second. The recovery recorded for zero time is obtained by extrapolating the median line of the trace back to zero time. Complete recovery in this case requires over 5 hours, which is not unusual for gum rubber. This time may appear long to those who work with rubber in the factory; but it must be remembered that in the factory rubber is usually allowed to cool after calendering or extruding, and it is subjected to mechanical restraint due to its own weight. Both of these factors tend to stop elastic recovery before all the internal stresses in the rubber are released.

In Fig. 8 are shown the elastic recovery curves for pale crepe, milled 30 minutes, obtained at  $80^\circ$  C. and  $135^\circ$  C. with annealing times of 0, 0.2, 2, and 20 seconds. It is seen that the recovery during the first 5 seconds is considerably reduced by annealing; but the additional recovery after 5 seconds is practically unaffected. The total recovery is less at the higher temperature and is attained more quickly.

#### Physical Constants in Oscillations

It is obvious that a modulus of rigidity and a coefficient of viscosity can be calculated from the frequency and damping factor of the wave form traced in the recovery curves. If we assume simple viscous damping, the free oscillations of the rotor are represented by

$$I(d^2\theta/dt^2) + f(d\theta/dt) + \beta\theta = 0, \quad (1)$$

in which  $\theta$  = angular displacement of rotor in radians,  $t$  = time,  $I$  = moment of inertia,  $f$  = viscous friction constant due to the rubber,  $\beta$  = torque constant due to the rubber.

The solution is

$$\begin{cases} \theta = Ae^{-f/2I}t \cos 2\pi\nu t \\ \nu = (1/2\pi) (\beta/I - f^2/4I^2)^{1/2}. \end{cases} \quad (2)$$

Therefore, it can readily be shown that

$$\begin{cases} f = 4\pi\nu Ik, \\ \beta = 4\pi^2\nu^2 I(1 + k^2), \end{cases} \quad (3)$$

where

$$k = (1/2\pi\nu) \log (\theta_0/\theta_n),$$

$\theta_0$  and  $\theta_n$  being the initial amplitude and the amplitude after  $n$  complete oscillations, respectively.

The relationships between  $f$  and  $\beta$  and the physical constants of the rubber are obtained by applying the formulas in the previous reference,<sup>6</sup> bearing in mind that the relationship between modulus of rigidity, angle of displacement, and torque corresponds exactly to the relationship between coefficient of viscosity, angular speed of rotation, and torque. The following relationships are easily deduced:

$$\begin{cases} f = 4\pi l\eta_0 R_1^2 R_2^2 / (R_2^2 - R_1^2), \\ \beta = 4\pi l\mu R_1^2 R_2^2 / (R_2^2 - R_1^2), \end{cases} \quad (4)$$

in which  $l$  = effective length of rotor or stator,  $R_1$  = radius of rotor,  $R_2$  = radius of stator,  $\eta_0$  = coefficient of viscosity in oscillation,  $\mu$  = modulus of rigidity.

From Equations (3) and (4), the dimensions of the rheometer and the speed of the stylus it is found that

$$\begin{cases} \eta_0 = 7.7 \times 10^3 k, \text{ poises,} \\ \mu = 1.00 \times 10^6 (1 + k^2/\lambda) \text{ dynes per sq. cm.} \end{cases} \quad (5)$$

$\lambda$  being the wave-length in the recovery tracing.

From Equations (5) the following values were calculated for a sample of well-masticated smoked sheet at 97° C.:

Previous Driving Wt., Lb.	$\eta_0$	$\mu$
50	$1.10 \times 10^3$	$2.66 \times 10^6$
90	$1.46 \times 10^3$	$2.66 \times 10^6$

The viscosity of this same sample measured under continuous rotation is very much higher:

Driving Weight	$\eta$
Kg. Lb.	
4.5 10	$2.9 \times 10^7$
36.3 80	$2.3 \times 10^8$

The modulus of rigidity is somewhat less, but of the same order of magnitude as that of soft vulcanized rubbers at room temperature.

Attempts were made to determine the elastic stress in the rubber at the moment of release by measuring the curvature at the knee of the autographic recovery curve. The measurements obtained were too erratic to be of any value. The difficulty lay in the disturbing vibrations set up in the apparatus by the clutch releasing mechanism. Possibly a clutch and quick release mechanism could be

Trace No.	W, Driving Wt. Kg. Lb.	$t_a$ , Annealing Time (Sec.)
1	36 80	0
2	22 50	0
7	22 50	2

designed to eliminate this trouble, but the problem does not appear easy. The fly-wheel at the bottom of the rotor shaft was added with the purpose of increasing the period of oscillation and extending the knee beyond the duration of the disturbing vibrations; but a much larger fly-wheel would be required to accomplish the purpose.

The experimental data that have been reported here are not very precise, but at least they show that an instrument has been devised which successfully measures the fundamental rheological properties of raw rubber. Greater precision doubtless can be obtained; but high precision would probably be wasted on rubber, which varies so much with time and with previous treatment. The essential features of viscosity and elastic recovery have been developed. The relationships revealed are quite complicated, and no theories so far developed will explain the complete rheological curve and its variation with temperature, or the peculiar form of the elastic recovery curve.

#### References

- <sup>1</sup> Peek, *J. Rheology*, **3**, 345 (1932).
- <sup>2</sup> Scott, *Trans. Inst. Rubber Ind.*, **10**, 481 (1935).
- <sup>3</sup> Peek and Erickson, *J. Rheology*, **2**, 351 (1931).
- <sup>4</sup> Mooney, *Ind. Eng. Chem., Anal. Ed.*, **6**, 147 (1934). Also U. S. Pat. 2,037,529, Mar. 14, 1936.
- <sup>5</sup> M. Mooney, *J. Rheology*, **2**, 210 (1931).
- <sup>6</sup> Reference No. 3, *Ibid.*, **2**, 210 (1931).

# A Preliminary Study of the After-Effect or Drift in Rubber under Constant Load

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## Introduction

When a suitable weight is supported by suspension from a piece of rubber, as a stationer's band, the rubber may be stretched any amount up to several times its original length, but its new length is not constant; it increases with time. The increase in length with time is variously known as "after-effect," "creep," "drift," "flow," or "time-yield." This phenomenon, which seems to have been very incompletely investigated, was probably first recognized by Dietzel<sup>1</sup> in 1857. Kohlrausch<sup>2</sup> in 1875 made an extensive study of both torsional and linear after-effect in metal, glass, and rubber. The loads used by Kohlrausch on rubber were, however, exceedingly small, and the duration of drift was limited to one day. He came to the conclusion that drift in rubber followed a power law for the first sixty minutes. During the next decade Pulfrich<sup>3</sup> slightly extended the work of Kohlrausch by experimentation on a red rubber tube, using elongations up to 150 per cent, with maximum observation time of 15 days. He concluded that the power law of Kohlrausch held for at least thirty minutes of drift. In 1903, Bouasse and Carrière<sup>4</sup> observed the after-effect (in pure gum and sulfur cords of 4 mm. diameter and of specific gravity 0.984) under a great variety of experiments, and concluded that drift was to be expressed by an exponential or logarithmic law rather than by a power function. Both Phillips<sup>5</sup> and Schwartz<sup>6</sup> arrived at similar conclusions. More recently Ariano<sup>7</sup> reported that the drift proceeded at a decreasing rate which finally assumed a constant value either finite or zero. Van Geel and Eymers<sup>8</sup> found that for milled rubber the drift continued until the specimens broke, but that for rubber obtained by evaporation of latex all after-effect ceased within three minutes. Shacklock<sup>9</sup> noted that creep took place for some hours and then reached a limit. Evidently more light needs to be cast on the problem of the drift effect in rubber. Two preliminary experiments on drift are herein considered; Part I on general trends, and Part II on more specific analysis of the effect as observed in one specimen.

## Part I. Experimental

Twelve selected rubber bands were hung from metal hooks screwed into the ceiling of an apparatus cabinet, the shelves of which had been removed. Specially prepared indicator hooks linked the bands to their respective load carriers. The increasing length of the bands was observed day by day through the closed glass doors of the cabinet by means of a meter scale. A plane mirror behind the pointers enabled observations to be made without parallax to tenths of millimeters. The specimens were shielded from strong light. They were subjected to room temperature fluctuations, but readings in this experiment were taken only when the thermometer hanging with the bands showed 27.0° C. (the temperature of the room being altered when necessary in order to attain this figure). Eleven of the specimens were no. 50 two-inch stock bands furnished through the courtesy of

The B. F. Goodrich Company, and "made from very high grade rubber gum, with the addition of only such ingredients as are necessary to produce a vulcanized rubber band of highest grade." These bands were approximately  $1.5 \times 1.5$  mm. in cross-section and, when stretched by a 53 g. tension between two pins to the extent that all slack was taken up, averaged about 5 cm. in length. The remaining specimen was a ring about  $1 \times 4$  mm. in cross-section and about 31.8 mm. inside diameter made of pure gum vulcanized in a mold at the National Bureau of Standards. The respective loads were placed on the hangers while the hangers were held in position with supporting fingers from beneath, the hand then being slowly lowered. Each specimen was given from 10 to 12 seconds during which to accept responsibility for the full magnitude of the load. This time element was provided in order to allow the bands to be stretched more or less isothermally. To obtain a reading of the length of the band at the instant of acceptance of the load was not always possible, but it was possible to obtain fairly reliable readings after 20 seconds from the beginning of the drop. The twelve bands were stressed as follows: 3 with 350 grams, 4 (including the molded specimen) with 550 grams, 3 with 750 grams and the remaining 2 with 1000 grams. Triplicate loads were chosen in order to determine the significance of individual differences in specimens under the same factors.

TABLE I  
BREAKING TIME IN DAYS FOR RUBBER BANDS UNDER VARIOUS CONSTANT LOADS AT  
27° C.

Band Number	Original Length, $l_0$	Constant Load	Life in Days	Average Life
1	5.00 cm.	350 g.	252 da.	
2	4.95	350	240	
3	5.20	350	228	240 da.
4	4.95	550	195	
5	5.05	550	203	
6	4.80	550	228	209
7	5.15	550	115	
8	5.00	750	202	
9	5.10	750	203	
10	4.95	750	302	236
11	5.00	1000	315	
12	5.15	1000	228	271
Average	5.02		226	239
Median	5.00		228	238
Mode	5.00		228	

A dial hygrometer placed within the cabinet showed that, although relative humidity was not constant, as far as could be determined its normal variation had no effect upon the drift. The effect of temperature on the length of the bands, however, was very marked. Observations on this effect will be dealt with in a separate paper. Cords, tubes, or strips of rubber doubtless would have provided specimens of more uniform cross section, but bands were chosen because of simplification of the grip problem.

### Results

Observations of the lengths of the bands at 27.0° C. were made daily, or every few days, until the last band was found broken on the 316th day. The ring band (No. 7) had the shortest life, having broken on or about the 115th day. The

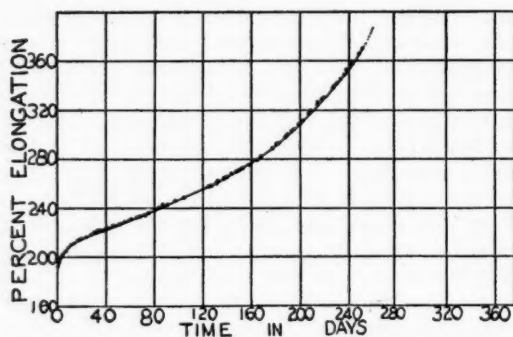


Figure 1—350 Grams' Tension

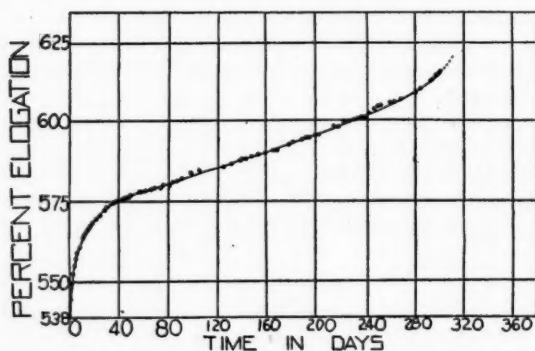


Figure 2—750 Grams' Tension

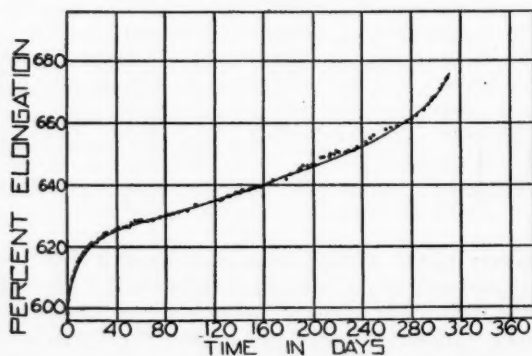


Figure 3—1000 Grams' Tension

Figures 1-3—Drift in Rubber under Constant Tension at 27° C.

life of the other bands ranged from 195 to 315 days as shown in Table I. It is interesting to note that the distribution of the lives of the 12 bands showed an average of 226, and both a median and a mode of 228 days. The latter statement is not altered by considering only the 11 similar bands, but the average life of the



set is then increased 10 days. There seems to be no correlation between the load and the time that the specimen can support a given load.

By the term elongation in this experiment is meant the increase in length,  $e$ , beyond the original length,  $l_0$ , of the specimen. That is, with  $l$  representing the length of the band at a given time,

$$l = l_0 + e.$$

The variation of the several elongations with time is shown in Figs. 1 to 3, which present graphs of representative specimens for each load. Curves for the other specimens were similar, though not identical. These figures indicate that in each

TABLE II

DRIFT IN RUBBER BANDS AS INDICATED (A) BY TIME CHANGE IN PERCENTAGE ELONGATION,  $E = (e/l_0) 100$  AND (B) BY CHANGE IN YOUNG'S MODULUS,  $M = (F/a_0)/(e/l_0)$  IN DYNES PER SQ. CM., AT DIFFERENT TIME INTERVALS UNDER VARIOUS CONSTANT LOADS AT 27° C.  $a_0 = 2 (1.5 \times 1.5)$  SQ. MM.

Time under Constant Stress	350				Constant Load in Grams				1000			
	<i>E</i>	<i>M</i>	<i>E</i>	<i>M</i>	<i>E</i>	<i>M</i>	<i>E</i>	<i>M</i>	<i>E</i>	<i>M</i>	<i>E</i>	<i>M</i>
10 sec.	165	462 $\times 10^4$	322	372 $\times 10^4$	455	359 $\times 10^4$	526	414 $\times 10^4$				
1 min.	170	448	329	364	475	344	547	397				
10 min.	180	423	342	350	501	326	568	383				
1 hr.	184	414	354	339	519	315	580	375				
1 day	192	397	400	300	544	301	598	364				
10	208	366	440	272	554	296	615	352				
20	214	356	452	265	568	288	620	351				
40	223	342	465	258	576	284	625	348				
60	230	332	473	254	580	282	628	346				
80	239	319	479	250	582	281	630	345				
100	247	309	481	249	585	280	631	344				
125	256	297	488	246	587	278	634	343				
150	271	281	493	243	591	276	639	341				
190	300	254	502	239	596	272	645	337				
240	354	215	...	...	604	271	652	334				
300	...	...	...	...	618	264	668	326				
Break	371	205	515	233	619	264	680	320				
Inflection	226	337	485	247	584	270	630	345				
Breaking Time	252 da.		228 da.		302 da.		315 da.					
Inflection Time	50		110		100		80					
Band No.	1		6		10		11					
Unstressed Length, $l_0$	5.00 cm.		4.80 cm.		4.95 cm.		5.00 cm.					

case the elongation of the band increased continually from the time of application of the load to the time of breaking of the band. The drift never ceased. In Table II the percentage elongation for four representative bands is given for 16 arbitrarily chosen durations. In this table is also given an approximation of Young's modulus based on the cross-section,  $a_0$ , of the unstretched specimen. The problem of the selection of specimens of uniform original cross-section was not completely solved, and it is assumed that for this reason irregularities necessarily exist in the figures for the modulus, as shown in Table II. If it is legitimate to use the phrase, Young's modulus, for a coefficient defined as the constant load in dynes multiplied by the ratio  $l_0/a_0$  and divided by the variable  $e$ , then the modulus,  $M$ , itself, becomes, with  $e$ , a function of the time of drift. Templin and

Sturm<sup>10</sup> seem to use it in this functional way. (Froman<sup>11</sup> discusses Young's modulus as a variable.)

Figures 1 to 3 indicate not only that the drift effect was continuous, but also that its rate was neither constant nor uniform. For the rubber used in this experiment, the rate of drift began comparatively high, decreased to a minimum greater than zero, and then gradually but definitely increased until finally the band gave way. The inflection was so gradual that it might easily have been misinterpreted as a constant rate for some tens of days in the region centering roughly about the second or third month. As time went on, however, the increase in the rate became unmistakable. Table III presents, for different times, the magnitude of the rate of drift as determined by the tangent to the elongation curve at the respective time points. The minimum rate (that at the inflection point) was located at about 50, 110, 100, and 80 days, respectively, for the four specimens. There was thus no correlation between the load and the locus of the inflection point. The rate of drift in the vicinity of the breaking point is of course an accidental function, and statistically may be considerably higher than shown.

The positively accelerated portion of the drift may plausibly be explained by oxidation or other deterioration of the rubber. Not even for the smallest load, however, was the phenomenon of cracking or of any other change observable with a magnifying lens slowly moved along the stretched bands during the latter part of their lives. Furthermore, in no case did a specimen break from a gradual tear. Each band seemed entirely homogeneous until the final snap, and the break usually occurred at a supporting hook rather than at a weld or other point of low resistance in the band. Should a plasticization effect take place in rubber subjected to prolonged tension, it is quite thinkable that the line of drift may not merely curve upward during the latter days of the specimen, but that under suitable conditions it may eventually rise asymptotically as the breaking point is reached.

## Part II. Experimental

In order to investigate more thoroughly the early stages of the drift curve, the frame of a usual laboratory type of Hooke's law apparatus was used to support vertically a  $1 \times 65$  cm. glass tube, wound with 7 turns per cm. of No. 27 Nichro resistance wire, held coaxially in a 2 cm. glass jacket to shield it from convection currents and from extraneous temperature gradients. In the inner bore there was suspended a specimen rubber band in such a manner that at its fully stretched length it was well within the constant temperature region of the chamber. A long mirror scale was placed vertically in juxtaposition with a pointer fastened to the wire which linked the specimen to its load. Readings were readily estimated to

TABLE III  
RATE OF DRIFT,  $\Delta\epsilon/\Delta t$ , IN PERCENTAGE ELONGATION PER DAY AT SELECTED TIMES FOR RUBBER BANDS UNDER VARIOUS CONSTANT LOADS AT 27° C.

Time Point, $t$	Constant Load in Grams			
	350	550	750	1000
5th day	1.44%/da.	2.60	1.74	1.46
10th	0.95	1.64	0.94	0.93
20th	0.50	0.88	0.51	0.38
60th	0.39	0.31	0.13	0.12
100th	0.43	0.21	0.12	0.12
200th	0.99	0.31	0.15	0.15
Breaking Point	1.20	0.41	0.49	1.00
Minimum Rate	0.36	0.20	0.12	0.11

tenths of millimeters. Parallel with the specimen chamber there was a similarly constructed calibration or temperature observing chamber connected in the same electrical circuit as that of the specimen tube. The load was applied to the specimen manually with a 20 second interval for the drop. A reading of the length of the band was taken at the instant of acceptance of the full value of the load, and thereafter at variously dispersed intervals throughout the three-week period of the strained life of the band. The specimen was a No. 14 gage Goodrich band.

### Results

Figure 4 is a graph of the data taken in the second part of the experiment. A 6.12 cm. band was subjected to a constant load of 300 g. at 40° C. (The tempera-

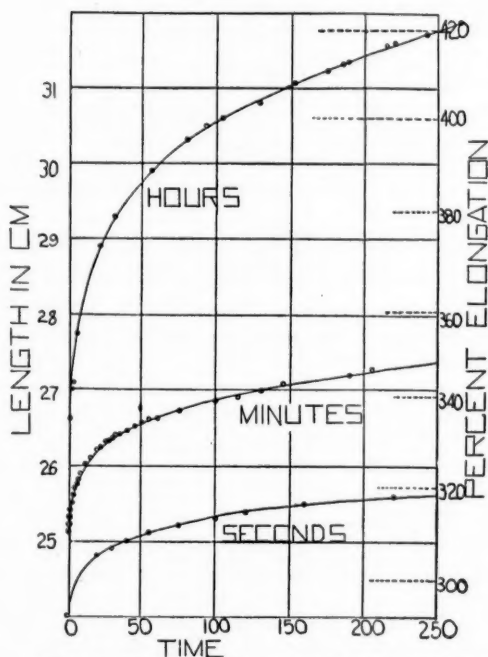


Figure 4—Drift in Rubber under Constant Tension of 300 G. at 40° C.  $L = 23.64 + 0.84 \log t$ , where  $30 < t < 7000$  Seconds.  $L = 24.00 + 2.66 t^{0.105}$ , where  $1 < t < 500$  Hours

ture varied a few degrees from this figure during the course of the experiment, but all readings were taken at 40° C.) The drift curve was plotted to each of three different time scales, viz., seconds, minutes, and hours. Although the graph seemed quite uniform and consistent, it appeared upon analysis that its mathematical expression required two distinct functions, one a logarithmic function governing the early portion of the curve, say between 30 and 5000 seconds from the time of acceptance of the load, and the other a power law covering the whole drift effect from about the 80th minute to the breaking point which occurred on the twentieth day, before a drift inflection could take place. These two empirical functions are, for the respective early and latter time periods,

$$l = l_0 + e_0 + e_t$$

$$= 6.12 + 17.52 + 0.84 \log t \quad 30 < t < 7000 \text{ sec.} \quad (1)$$

$$= 6.12 + 17.88 + 2.66t^{0.195} \quad 1 < t < 500 \text{ hr.} \quad (2)$$

where  $l$  is the length in cm. of the specimen at time  $t$ ,  $l_0$  its original unstretched length,  $e_0$  the elongation in cm. produced by the application of the load,  $e_t$  the drift or additional elongation in cm. at time  $t$ , and where  $t$  is the time measured from the moment of acceptance of the full load by the band. In Eq. (1)  $t$  is measured in seconds while in (2) it is measured in hours.

The very nature of the log law indicates that it of itself cannot be a complete expression for the phenomenon. Yet it is interesting to note that when used for the beginning of the curve, the average deviation for the 30 readings between 30 and 6000 seconds is only  $\pm 0.016$  cm. The average deviation from the power law for the 94 observations between 1 and 500 hours is  $\pm 0.045$  cm. These deviations are well within experimental error in the taking of the observations.

### References

- <sup>1</sup> Dietzel, *Polytechnisches Zentralblatt*, **1857**, 689-94; *Fortschr. Phys.*, 143 (1857); Todhunter and Pearson, "History of the Theory of Elasticity," Vol. II, Part I, 752.
- <sup>2</sup> Kohlrausch, *Ann. Physik*, **155**, 579 (1875); **158**, 337 (1876).
- <sup>3</sup> Pulfrich, *Ann. Physik*, **28**, 87 (1886).
- <sup>4</sup> Bouasse and Carrière, *Ann. Faculté des Sciences de Toulouse* [5], **2**, 285 (1903).
- <sup>5</sup> Phillips, *Phil. Mag.*, **9**, 513 (1905).
- <sup>6</sup> Schwartz, *J. Inst. Elec. Eng.*, **44**, 693 (1910).
- <sup>7</sup> Ariano, *India-Rubber J.*, **76**, 207 (1928); **78**, 316 (1929); *RUBBER CHEM. TECH.*, **3**, 62 (1930.)
- <sup>8</sup> Van Geel and Eymers, *Z. physik. Chem.* [3], **3**, 240 (1929); *Rubber Age*, **29**, 9 (1929); *RUBBER CHEM. TECH.*, **2**, 545 (1929).
- <sup>9</sup> Shacklock, *Trans. Inst. Rubber Ind.*, **3**, 568 (1933).
- <sup>10</sup> Templin and Sturm, *Proc. Am. Soc. Testing Materials* [II], **31**, 882 (1931).
- <sup>11</sup> Froman, *Phys. Rev.*, **35**, 264 (1930).

## Studies on the Joule Effect of Rubber

### II. Thermal Effect on Stretched Latex Vulcanizates

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Various methods, apparatus, and patents concerned with the application of latex, and many papers on the colloid chemistry of latex have been published. However, there has been little physico-chemical research on latex vulcanizates, and the fine structure of the vulcanizates and the effects of vulcanizing agents, accelerators, fillers, stabilizers, etc., have not been thoroughly investigated. The authors have reported on the Joule effect of vulcanized rubber prepared from milled pale sheet by the usual process, and have discussed the relation between this effect and the properties of the vulcanizates (*J. Soc. Chem. Ind., Japan*, 37, 522B (1934)). The present paper is concerned with the same experiments performed with vulcanized films prepared from latex.

#### 1. Preparation of Samples and Experimental Procedure

The vulcanizate was prepared from ammonia-preserved latex containing 36.8% rubber by compounding with colloidal sulfur, zinc oxide, accelerator, and casein. The sample used for the present study was made by immersing in the compounded latex a test tube, removing the tube, drying, redipping as many times as required, and heating the test tube, with its dried deposit on the surface, in a hot-air chamber at 120° C. After drying and vulcanizing, the rubber film was removed from the mold, and was cut to give a ring 10 mm. wide, with inner diameter of 13 mm. and thickness of about 1 mm. The experimental procedure was almost the same as described in the previous paper, *i. e.*, the ring-shaped specimen was placed in an air thermostat at 25° C. and stretched under tensions of 5, 10, and 15 kg. per sq. cm., respectively. The elongation of the specimen under these tensions was measured by a cathetometer, and the ratios of the elongation to the original length are designated as "Elongation" in the following tables. Under these extensions, the specimens were heated in another water thermostat at 80° C. Heated in this way, the specimens elongated gradually a little. The ratios of these second elongations to the original lengths are noted as "Heating elongation." The water thermostat was then removed and the specimens were cooled to the temperature of the air thermostat of 25° C. By this cooling, considerable elongation was observed. When the specimen was again heated to 80° in the water thermostat, the heating elongation did not appear. On the contrary, a shrinkage almost comparable to the previous cooling elongation occurred. Thus, the first heating of a freshly prepared specimen produced an irreversible heating elongation, after which successive cooling and heating showed a reversible elongation and shrinkage, respectively. These reversible thermal effects may be assumed to represent a Joule effect. "Joule effect" in the following table is the ratio of the successive cooling elongation, which was observed after removing the sample from the water thermostat, to the original length.

*Experiment I. Influence of Casein Content.*—In the preparation of a uniform film of latex vulcanizate, the use of a proper protective colloid is necessary. Various protective colloids and stabilizers have been described (cf. R. J. Noble, "Latex in

Industry," New York, 1936, p. 130). In our experiment, a uniform film which absorbs water as little as possible when immersed in the water thermostat of 80° C. was necessary. Casein was used as a protective colloid for this purpose. The following table shows the influence of casein content on the stiffness and resistance to water of a latex vulcanizate containing 100 parts of rubber, 0.8 parts of zinc oxide, 2 parts of colloidal sulfur, 1 part of Vulcacit P, and various amounts of casein. The compounded latex was cured in a hot air chamber at 120° C. for 20 minutes.

TABLE I

Casein Content	500% Modulus	Rate of Water Absorption (%)
1	10.3 kg. per sq. cm.	14.1
2	11.6	21.8
3	12.3	25.1
4	15.5	58.0

The rate of water absorption was calculated by dividing the weight increase of the specimens after immersion in boiling water for 10 minutes, by the original weight. As shown in the above table, the higher the casein content the greater the water absorption.

*Experiment II. Influence of Sulfur Content.*—All the physical properties of rubber vulcanizates are influenced by the sulfur content and curing time. To investigate their influence on the Joule effect, specimens were prepared from the same compound used in the above experiment, containing one part of casein and various parts of sulfur, curing for 30 minutes. As sulfur increases stiffness, the experiments on the Joule effect were performed under three tensions, namely, 5, 10, and 15 kg. per sq. cm., in which 15 kg. per sq. cm. is almost the tensile strength.

TABLE II

Tension (Kg. per Sq. Cm.)	Sulfur Content	Elongation (%)	Heating Elongation (%)	Joule Effect (%)
5	0.5	406.3	275.6	17.5
	1	358.8	158.8	125.2
	2	282.1	124.7	116.3
	4	180.0	83.4	67.0
	5	145.6	50.9	63.7
	6	130.7	38.1	28.4
10	0.5	650.4	321.4	41.1
	1	316.6	148.1	202.9
	2	449.5	161.7	191.7
	4	239.6	64.3	143.9
	5	217.3	63.5	140.5
	6	197.8	48.5	49.4
15	0.5	break down		
	1	692.3	258.3	213.7
	2	460.7	180.6	236.2
	3	351.6	151.3	196.5
	5	268.3	70.7	120.0
	6	255.0	103.6	74.6

The relation between Joule effect and sulfur content under various tensions is shown in Fig. 1.

*Experiment III. Influence of Time of Cure.*—For a thorough investigation, samples containing various sulfur contents should be cured for different times and their elongations and Joule effect under several tensions be observed. However, it is too laborious and expensive to attempt such experiments. Hence, a



sample containing one part of sulfur cured for various times at 120° C. was tested in the following experiments under a tension of 10 kg. per sq. cm.

TABLE III

Time of Cure in Minutes	Elongation (%)	Heating Elongation (%)	Joule Effect (%)
10	353.3	195.8	220.7
20	310.7	128.2	183.4
30	285.7	155.8	195.5
40	290.6	50.8	138.5

## 2. Discussion

The results of the experiments may be summarized as follows.

1. By heating and cooling the stretched latex vulcanizates, the same phenomena,

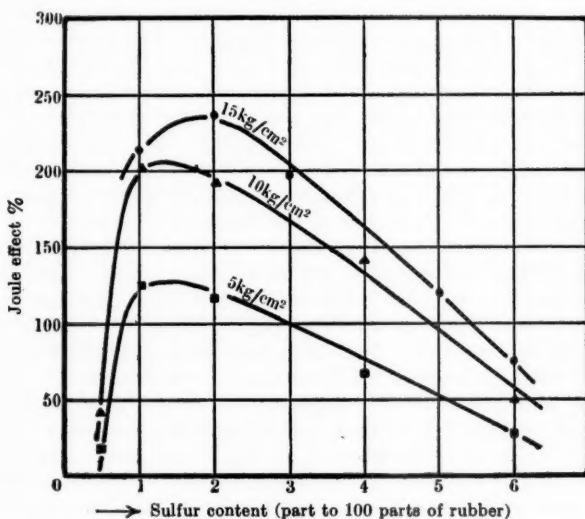


Figure 1

namely, elongation, heating elongation, and Joule effect observed in the previous experiment on vulcanized rubber from pale sheet, were observed.

2. Consequently, with increase of sulfur content, the elongation and heating elongation diminish. The Joule effect showed a maximum point when the sulfur content was about one part per 100 parts of rubber.

3. With increasing time of cure, the vulcanizates became stiffer, and their elongations, heating elongations, and Joule effect diminished.

4. The greater the tension the greater the elongation, heating elongation, and Joule effect.

To explain fully these results from the physico-chemical point of view may be difficult. The following presumption seems, however, to be highly probable. In a previous paper, the irreversible elongation by the first heating was assumed to be caused by an internal stress in fresh vulcanized rubber resulting from the milling effect and other effects. A similar heating elongation appeared also in the latex vulcanizates which had not been milled at all. It may therefore be assumed that

stresses exist in latex vulcanizates prepared from latex compounds consisting of rubber globules of irregular shape, filler, sulfur, casein, accelerator, and serum. The polydispersoid is dried on the solid surface of the mold, producing a stiff film. During drying and vulcanization, the rubber globules are under irregular tensions. Thus, it is probable that the fresh latex-vulcanizate is also under considerable stress. By stretching this vulcanizate in a hot air chamber, the stress disappears, and all micelles become oriented along the direction of the tension. This may be a cause of the "heating elongation" of latex vulcanizates. The increased tension is able to remove more inner stress, so the heating elongation increases with increase in tension. Increase of sulfur content and curing time stiffens the vulcanizates, and since the inner stress of the stiff vulcanizates cannot be removed easily, the heating elongation diminishes. In the previous paper, it was reported that the Joule effect of vulcanized rubber is most remarkable for samples which are properly vulcanized, and is not affected by disaggregation or depolymerization. The Joule effect of latex vulcanizates shows a similar tendency. Sulfur above 2 parts reduces the Joule effect. This may result from disaggregation or depolymerization of the rubber, and also from the increase of free sulfur which acts as a diluent of the Joule effect. Consequently with prolongation of the time of cure, disaggregation and depolymerization may occur to a considerable extent. Though vulcanization proceeds simultaneously, the former has more influence than the latter in reducing the Joule effect. These results are shown in Expt. III. In the previous experiments, the Joule effect of vulcanizates from pale crepe rubber and sulfur increased progressively with time of vulcanization, while vulcanizates containing rubber, sulfur, and diphenyl-guanidine showed the maximum Joule effect at a cure of 30 minutes; longer times diminished the effect. In this paper, by curing latex films for longer times than ten minutes, the effect diminished. This may have been caused by the fact that the latex compound contained an ultra-accelerator, such as Vulkacit P; at the same time the dried film of latex to be vulcanized was only about 1 mm. thick. It is very interesting that latex vulcanizates behave almost like ordinary vulcanized rubber. Disregarding the differences between latex vulcanizates and ordinary vulcanized rubber, the crystalline structure theory of stretched rubber explained by Hauser and others on the basis of x-ray studies may be applied to the present experimental results. The theory shows that the Joule effect is caused by the heat of crystallization of stretched rubber molecules. This crystallization is an intramicellar phenomenon. The factor above described which reduces the Joule effect may be chiefly disaggregation which occurs in the intermicellar space, whereas factors which increase the effect consist of combination of sulfur and rubber hydrocarbon, polymerization of the vulcanizate in the intramicellar space, and increase of the polar affinity of each micelle and molecule. A more detailed research on the structure of latex vulcanizates will be reported in the near future.

### 3. Summary

Latex vulcanizates behave with regard to the Joule effect similarly to ordinary vulcanized rubber when heated and cooled in a stretched condition. The observed thermal effect is assumed to represent the Joule effect. This effect is reduced chiefly by depolymerization and disaggregation of the rubber, and is increased by vulcanization, which may be followed by polymerization of vulcanized rubber molecules and an increase of the polar affinity of each molecule and micelle.

## Swelling and Solvation of Rubber in Different Solvents

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**T**WO principal explanations for the high viscosity of rubber sols have been advanced. Staudinger and co-workers (14) believe that rubber consists of extremely long, stiff, and extended molecules which, even in low concentration, interfere with one another during flow because of the large space required for the rotation of a single molecule. They recognize that a fiber molecule can be solvated (15, 17) but do not believe that the viscosity depends primarily on solvation (18). This explanation for the high viscosity of rubber solutions has been widely accepted since its introduction. Other investigators (1, 3, 4, 8, 10, 12) believe that rubber is micellar and probably solvated when dispersed in solvents. The solvated unit is usually considered to consist of a number of molecules more or less loosely bound into a group which becomes greatly swollen and in this manner removes a great portion of the liquid as an effective dispersing medium. According to Meyer and Mark, 1 gram of rubber in 100 cc. of benzene would imbibe solvent to produce a system containing 20 to 40 grams of solvated rubber in 80 to 60 cc. of free benzene. Hatschek believes the swollen units to be more or less mobile and easily deformed so that flow takes place in high concentration only by distortion of the solvated unit.

A close relation between the viscosity of rubber sols in various types of solvent and the swelling of rubber produced by the same solvents would indicate a micellar structure for rubber sols. The process of imbibition which involves forces small enough so that slight changes in the system (such as cooling) will often produce syneresis, could be expected to immobilize a considerable amount of liquid. The effect of this immobilization on viscosity would be that caused by both a decrease in the volume of solvent and an increase in the effective volume of dispersed material. Although a single molecule would not be expected to swell, it might immobilize a certain quantity of solvent by association. The viscosity of a molecular solution of low concentration of most materials is, however, usually little greater than the viscosity of the solvent.

Different solvents have been shown by Van Rossem (19), Kawamura and Tanaka (5), Sakurada and Tanaka (11),

and Philippoff (9) to produce sols of different viscosity. Kirchhof (6) noticed the difference in solvent power of benzene, gasoline, carbon tetrachloride, and various chlorinated acetylenes and also pointed out the parallel between swelling and solvent action. Hatschek noted from the data of Kirchhof that a relation existed between swelling power and relative viscosity. Fujihara (7) presented data which showed a large variation in the relative viscosity of rubber sols produced with carbon disulfide, benzene, chloroform, carbon tetrachloride, and trichloro- and tetrachloroethane. The difference in viscosity of rubber sols in the common solvents such as benzene and gasoline is small.

### Variation in Viscosity

The fractional increase in viscosity produced by rubber in a number of solvents has been found to vary within wide limits:

Pale crepe rubber was milled for 10 minutes on a warm mill to ensure solubility and uniformity of the sample. Ten grams of this rubber were made up to 500 cc. with solvent and shaken until dispersed. The solution stood for 6 to 10 days before being used. Lower concentrations of rubber were obtained by diluting portions of this 2 per cent cement, and in each case the diluted sample stood from 18 to 24 hours before being tested. The relative viscosity was determined at  $30^{\circ} \pm 0.1^{\circ}$  C. in an Ostwald type viscometer which flowed a volume of 7.2 cc. through a capillary 0.716 mm. in diameter and 4.5 cm. long under a mean head of 9.9 cm. of solution. All solvents and solutions were handled in clear glass in diffused daylight and no attempt was made to protect the material from oxygen.

The solvents were selected to represent a range from nonpolar to strongly polar types. In certain cases, such as nitrobenzene, a solution could not be prepared directly but the effect of the solvent was obtained by dilution of a more concentrated benzene sol. Benzotrifluoride was included because of the great similarity in the directing influence of the nitro and trifluoromethyl groups. Menthol was included because of the interest created by Pummerer and others in the determination of the molecular weight of rubber in this solvent. In order to avoid the excessive heating required to promote solution in menthol, a solution in mixed solvents was obtained by diluting a more concentrated benzene sol with menthol.

The time of flow is shown in Table I to differ considerably for each solvent and solution. The variation in viscosity of sols of low concentration is almost in proportion to the variation between the solvents. The same general tendency is shown at the highest concentration, but chlorobenzene and dibutylamine fall somewhat out of line.

The fractional increase in viscosity  $[(T \text{ solution}/T \text{ solvent}) - 1]$ , which at any fixed low concentration should, according to the formula of Staudinger (16), be proportional to the molecular weight or chain length of the rubber molecule is shown in Table II and Figure 1. These data show that the fractional increase in viscosity decreases continually with decreasing concentration and at no low concentrations do the values approach constancy. The value obviously becomes zero at

zero concentration. These data agree with the findings of Zhukov, Komarov, and Gribova (21) for sodium butadiene rubber, sodium isoprene rubber, and chloroprene polymer. The fractional increase in viscosity at any fixed concentration varies with the nature of the solvent. This is in contrast to the statement of Staudinger (13) that the solvent is without significant influence. Such results show that the effective size of the dispersed rubber particle, whether molecular or micellar, is not constant in all dilute solutions but is different in each solvent. If the fractional increase in viscosity is caused directly by unsolvated molecules, then certain sol-

TABLE I. TIME OF FLOW OF RUBBER SOLUTIONS AT 30° C.

Solvent	Grams Rubber per 100 Cc. Soln.:							
	0	0.095	0.125	0.25	0.375	0.5	0.75	1.0
Time of flow, seconds								
Chlorobenzene	71.1	81.7	85.8	102.6	129.6	156.8	235.0	321.7
Benzene	70.6	81.7	84.7	103.8	128.9	153.7	224.5	294.5
Gasoline	79.1	88.2	93.4	106.0	134.6	157.5	230.4	303.5
Dibutylamine	104.3	117.2	120.5	138.6	161.2	187.5	247.2	315.2
Amyl chloride	63.3	67.4	69.0	76.4	89.7	95.6	135.2	172.7
Caproic acid	292.0	307.5	326.5	349.1	393.1	430.0	535.5	651
Ether	44.4	47.1	48.1	52.3	57.9	62.5	76.8	96.0
Benzotrifluoride	53.7	56.7	57.4	61.7	66.8	73.5	87.6	106.7
1 vol. benzene plus:								
2 vol. nitrobenzene	102.1	106.7	108.0	112.0	125.6	130.9	165.2	200.5
4 vol. menthol	513.6	...	...	695	...	...	1257	...

TABLE II. FRACTIONAL INCREASE IN VISCOSITY OF RUBBER SOLUTIONS

Solvent	Viscosity of Solvent Sec.	Grams Rubber per 100 Cc. Soln.:							
		0.095	0.125	0.25	0.375	0.5	0.75	1.0	2.0
		Fractional increase in viscosity							
Chlorobenzene	71.1	0.15	0.21	0.44	0.82	1.20	2.30	3.52	12.27
Benzene	70.6	0.16	0.20	0.47	0.82	1.18	2.17	3.17	11.41
Gasoline	79.1	0.12	0.18	0.34	0.70	0.99	1.92	2.84	10.25
Dibutylamine	104.3	0.12	0.15	0.33	0.54	0.80	1.37	2.02	6.29
Amyl chloride	63.3	0.06	0.09	0.20	0.42	0.51	1.12	1.72	6.74
Caproic acid	292.0	0.05	0.12	0.20	0.35	0.47	0.83	1.23	3.60
Ether	44.4	0.06	0.08	0.18	0.30	0.41	0.73	1.16	4.21
Benzotrifluoride	53.7	0.05	0.07	0.15	0.25	0.37	0.63	0.98	3.61
1 vol. benzene plus:									
2 vol. nitrobenzene	102.1	0.044	0.06	0.10	0.23	0.28	0.62	0.96	3.34
4 vol. menthol	513.6	..	..	0.35	..	..	1.45	..	6.62

vents must bring about a decrease in molecular size of the rubber. This appears unlikely when chemically inactive solvents are used.

In Table II the fractional increase in viscosity bears no relation to the viscosity of the solvent. If the increase in viscosity is due only to the length of a rigid filiform molecule, the percentage increase should either be uniform in all solvents or vary as some function of the viscosity of the solvent. Since no relation is obvious between the increase in viscosity and the viscosity of the solvent, it must be concluded that the viscosity is controlled by some factor other than the size and shape of the rubber molecule.

The fractional increase in viscosity according to the formula of Staudinger is directly proportional to the molecular weight

when a fixed low concentration is considered. When applied to this formula, the data in Table II indicate that the molecular weight of the same rubber varies as much as 300 per cent under the influence of different solvents.

Rubber is not degraded after being dissolved in a solvent which produces a low viscosity. After removing the solvent it is possible to replace it with another and thus obtain a viscosity characteristic of the second solvent. This process can be repeated a number of times if the rubber is protected from oxidation.

Two grams of milled pale crepe rubber were made up to 100 cc. with solvent in a distilling flask and shaken until the solution was homogeneous. Milled rubber was used because the viscosity

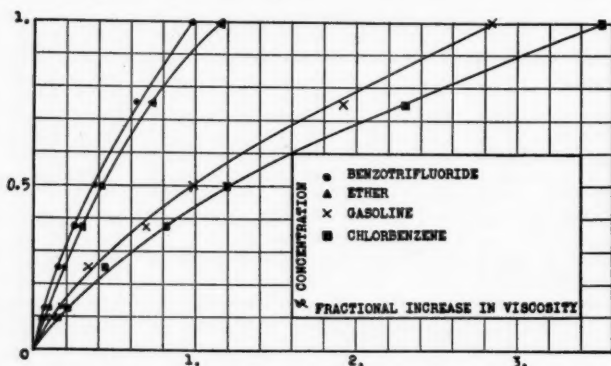


FIGURE 1. FRACTIONAL INCREASES IN VISCOSITY OF RUBBER SOLUTIONS

of its solutions is less influenced by subsequent oxidation. The viscosity was determined at 30° C. after standing for 24 hours and the contents of the viscometer were then rinsed into the distilling flask with pure solvent. The solvent was removed from the rubber by heating to a final temperature of 45° to 50° C. under a pressure of 1 mm. An equal volume of the second solvent was then added to the flask which was flushed with nitrogen and shaken to promote solution. This process was repeated with each solvent. The results of such tests are shown in Table III and indicate that rubber is not changed in any manner by being brought into solution but reaches a definite equilibrium with each solvent.

### Variation in Swelling

Swelling tests were made on both vulcanized and unvulcanized rubber.

Smoked sheet rubber containing 10 per cent sulfur was vulcanized for 60 minutes at 145° C. Strips of rubber 1 mm. square and 2 cm. long were cut from the center of the vulcanized slab in a manner which eliminated the surface of the rubber that had been in contact with the mold. Similar strips were prepared from unmilled smoked sheets and from a sheet prepared by the evaporation of a latex which had been concentrated by centrifug-



ing. The strips were placed in glass tubes with 10 cc. of the solvent, and the length was followed by measuring through the glass. Equilibrium was reached more rapidly with the less viscous solvents but in all cases it was essentially complete in 24 hours. The length was somewhat difficult to determine ac-

TABLE III. VISCOSITY CHANGES CAUSED BY REPLACING ONE SOLVENT WITH ANOTHER

Order	Solvents	Viscosity Sec.	Solvents	Viscosity Sec.
Original	Ether	212	Benzotrifluoride	245
2	Benzene	715	Chlorobenzene	836
3	Ether	231	Benzotrifluoride	222
4	Benzene	730	Chlorobenzene	798

TABLE IV. SWELLING POWER AND VISCOSITY

Solvent	—2% Solution— Fractional		Vol. of 1 Cc. at Max. Swelling, Cc.		
	Viscosity, seconds	increase in viscosity	Evapo- rated latex	Sheets	Vulcanized rubber
Chlorobenzene	944	12.27	37	28	9.8
Benzene	876	11.41	30	13	8.4
Gasoline	891	10.25	33	10	5.4
Dibutylamine	782	6.29	21	9	8.0
Ether	232	4.21	14	4	3.9
Caproic acid	1334	3.60	10	8	4.1
Benzotrifluoride	248	3.61	8	7	3.1

curately with the unvulcanized rubber, especially in benzene and chlorobenzene. The portion of the rubber which diffused into the solvent undoubtedly influenced the final length both by loss of rubber and by reducing the swelling maximum due to the presence of dissolved rubber as shown by Blow and Stamberger (2). In most cases the edges of the strips were well defined after 24 hours, when the final readings were made. The measurements are sufficiently accurate to determine differences in swelling in a roughly quantitative manner. Volume swelling was calculated on the assumption that the swelling was equal in each dimension.

The results of these measurements are shown in Table IV compared with the viscosity data for the 2 per cent solution from Tables I and II. The data agree in general with the observation of Kirchhof (6) and Hatschek (3) that the best swelling agent produces a solution of the greatest viscosity. Although the actual viscosity depends on the viscosity of the solvent, the fractional increase in viscosity shows a close parallel with the swelling power of the same solvent for either vulcanized or unvulcanized rubber. Dibutylamine has an abnormal swelling action on vulcanized rubber in accord with the known effect of accelerators on rubber containing combined sulfur (20).

The swelling of rubber depends to a great extent on the state of oxidation of the rubber. Gel rubber will swell but does not readily dissolve in benzene in the absence of oxygen.<sup>1</sup>

<sup>1</sup> The sample of gel rubber in an evacuated tube with benzene is described in *IND. ENG. CHEM.*, 27, 1317-21 (1935) and *Rubber Chem. Tech.*, 9, 342 (1936). The rubber shown in Figure 1A has been kept in diffused light at room temperature for one year without the formation of a smooth solution.

The oxidation of rubber during milling reduces the swelling required to detach the final swollen unit of rubber and, by creating more points of cleavage, causes a decrease in the size of the resulting micelle. Rubber which has been milled sufficiently appears to dissolve from the surface with little swelling.

The difference in swelling power of liquids and the relation between swelling and viscosity is not confined to rubber sols. Solutions of chloroprene polymer have been found to act in a similar manner. The fractional increase in viscosity is, however, considerably smaller than that for rubber, being 2.39, 1.74, and 1.18 for a 2 per cent solution of chloroprene polymer in benzene, amyl chloride, and dibutylamine, respectively. The polymer was not soluble in ether or benzotrifluoride.

### Conclusions

The large variation of the fractional increase in viscosity of rubber sols and its lack of relation to the viscosity of the solvent indicates that the increase in viscosity is not due to rigid filiform molecules.

The ability to interchange solvents and obtain a viscosity characteristic of the solvent shows the existence of a reversible equilibrium between solvent and rubber.

The close relation between the maximum swelling and the fractional increase in viscosity of rubber in different solvents suggests that rubber sols contain swollen micelles of rubber. The extent of swelling and the viscosity depend on the equilibrium between solvent and rubber which, in turn, depends on the state of oxidation (or other suitable chemical attack) of the rubber.

A rubber sol becomes a gel at the concentration which immobilizes essentially all the solvent.

The relative viscosity of rubber sols of equal concentration in the same solvent is probably some function of the degree of solvation of the dispersed particles which is influenced by the degree of oxidation of the rubber. Viscosity is not a measure of the molecular weight.

### Literature Cited

- (1) Bary, P., *Compt. rend.*, **170**, 1388 (1920).
- (2) Blow and Stamberger, *Rubber Chem. Tech.*, **4**, 64 (1931).
- (3) Hatschek, E., *J. Phys. Chem.*, **31**, 386-90 (1927).
- (4) Kawamura, J., and Tanaka, K., *J. Soc. Chem. Ind. Japan*, Suppl. binding, **35**, 186-91 (1932); *Rubber Chem. Tech.*, **5**, 627 (1932).
- (5) Kawamura and Tanaka, *J. Soc. Chem. Ind. Japan*, **35**, 1866 (1932).
- (6) Kirchhof, F., *Kolloidchem. Beihefte*, **6**, 1-22 (1914); *Kolloid-Z.*, **15**, 30 (1914).
- (7) Fujihara, *J. Rubber Soc. Japan*, **3**, 220-2, 224-9 (1931); *Rubber Chem. Tech.*, **5**, 620 (1932).
- (8) Meyer and Mark, *Ber.*, **61**, 1946 (1928).
- (9) Philippoff, W., *Kautschuk*, **12**, 124 (1936).
- (10) Pummerer, R., *Ber.*, **60**, 2167 (1926).

- (11) Sakurada and Tanaka, *J. Soc. Chem. Ind. Japan*, **37**, 470 (1934).
- (12) Stamberger, P., *Kolloid-Z.*, **45**, 239-44 (1928).
- (13) Staudinger, H., "Die hochmolekularen organischen Verbindungen," pp. 57, 178, Berlin, Julius Springer, 1932.
- (14) *Ibid.*, p. 79.
- (15) *Ibid.*, p. 126.
- (16) Staudinger, H., *Z. angew. Chem.*, **45**, 276-92 (1932).
- (17) Staudinger and Moyen, *Kautschuk*, **12**, 159 (1936).
- (18) Staudinger and Nodzu, *Helv. Chim. Acta*, **13**, 1350-4 (1930); *Rubber Chem. Tech.*, **4**, 545 (1931).
- (19) Van Rossem, *Kolloidchem. Beihefte*, **10**, 108 (1918).
- (20) Williams, I., *Ind. Eng. Chem.*, **26**, 1191-3 (1934); *Rubber Chem. Tech.*, **8**, 102 (1935).
- (21) Zhukov, Komarov, and Gribova, *Sintet. Kauchuk*, **5**, 9-12 (1936).

# The Fine Structure of Crystallized Rubber

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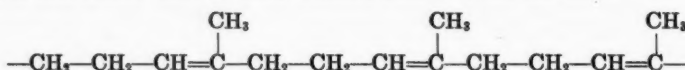
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Whereas in the unstretched state rubber gives on examination by x-rays the diagram of a liquid, in the stretched state it gives a well-defined fiber diagram. This was first described by Katz<sup>1</sup> in 1925.

Since that time the crystalline interferences of rubber have been studied by several investigators. The first classification of these interferences was undertaken by Hauser and Mark,<sup>2</sup> who arranged them in the form of a rhombic lattice.

Later, working with a thin film of highly stretched rubber, Mark and von Susich<sup>3</sup> succeeded in obtaining preparations with a higher degree of orientation. According to whether it was irradiated parallel or perpendicular to the surface of the film, such a preparation showed different intensities of the reflections. In this way Mark and von Susich succeeded in obtaining a different and more reliable indication of the reflections than did Hauser and Mark. Mark and von Susich found a rhombic elementary cell with axes of  $8.3 \pm 0.1$  A. U.,  $8.1 \pm 0.1$  A. U. (fiber axis), and  $12.3 \pm 0.1$  A. U.

On the basis of their better established elementary cell, Mark and von Susich developed a space model of rubber which agreed fairly well with the largest intensity effects. In constructing this model they relied on the assumption expressed by Meyer and Mark<sup>4</sup> that primary valence chains of the formula:



penetrate the entire crystallite in the direction of the fiber axis, and that lengthwise of the elementary cell there are two  $\text{C}_6\text{H}_8$  residues for every chain in the *cis*-position, and these are united in a diagonal spiral arrangement. Four such chains pass through the elementary cell, so that it contains eight residues.

Since the investigation by Meyer and Mark, photographic technic has advanced, and knowledge of atomic distances and valence angles of organic structures has been substantially increased and better defined, thanks chiefly to the numerous publications by Bragg and his collaborators.

Therefore, it seemed to us that the time had come to undertake a new study of rubber, particularly because several features in the work of Mark and von Susich have remained unexplained.

The number of  $\text{C}_6\text{H}_8$  residues in the cell, calculated from the experimental density of crystallized rubber, has been found to be 7.1 which is considerably different from the value of 8 required by crystallographic measurements. Furthermore, the reflection designated (040) does not conform to the lattice indicated. Finally, we believed that the chain structure described by them was no longer compatible with more recent data.

Accordingly with the aid of new highly monochromatic photographs, and the utilization of the data of Mark and von Susich on more highly oriented preparations, we undertook the problem of formulating an elementary cell which would

make it possible to classify all points and to establish a chain structure which is compatible with recent precise knowledge of distances and angles.<sup>5</sup>

1. *Technic.*—Various photographs of rubber samples were prepared. Nickel-filtered copper radiation was used, which, as evidenced by its spectrum, was very pure  $\text{CuK}\alpha$  radiation. To measure the distance, one photograph was taken with some powdered rock salt rubbed on a sample 0.2 millimeter thick. The distance between the sample and the plate was 41.0 millimeter, the screen had a diameter of 0.7 millimeter and a length of 80 millimeters.

The periods of the fiber axis were measured on the diatropes of the second layer line as  $8.20 \pm 0.05$  A. U., and the lattice plane distances corresponding to the first two equator reflections as  $8.47 \pm 0.05$  A. U. and  $12.57 \pm 0.05$  A. U. were in fair agreement with the corresponding values of Mark and von Susich. The  $\sin \theta$  values found and the intensities estimated on the photograph with the most points, which was made by Pankow (Fig. 1), are shown in Table I.

TABLE I

Point Equator	Sin $\theta/\lambda$	Estimated Intensity	hkl	Sin $\theta/\lambda$ Calculated
A <sub>1</sub>	0.079 <sub>3</sub>	strong	002	0.079 <sub>3</sub>
A <sub>2</sub>	0.118	very strong	200	0.118
A <sub>3</sub>	0.159	weak	004	0.159
A <sub>4</sub>	0.224	very weak	304	0.224
1. Layer Line				
I <sub>1</sub>	0.091	very weak	111	0.090 <sub>5</sub>
I <sub>2</sub>	0.100	strong	012	0.100
I <sub>3</sub>	0.133	fairly strong	210	0.133
			013	0.134
			211	0.134 <sub>5</sub>
I <sub>4</sub>	0.145	weak	211	0.142 <sub>5</sub>
			212	0.147
I <sub>5</sub>	0.175	very weak	114	0.174
I <sub>6</sub>	0.194	weak	312	0.195
			311	0.195 <sub>5</sub>
			214	0.196 <sub>5</sub>
2. Layer Line				
II <sub>0</sub>	0.122	medium	020	0.122
II <sub>1</sub>	0.135	weak	120	0.135 <sub>5</sub>
			121	0.139
II <sub>2</sub>	0.145	medium	121	0.143
			022	0.145 <sub>5</sub>
			220	0.170
			023	0.170 <sub>5</sub>
II <sub>3</sub>	0.166	weak	221	0.171
			221	0.177 <sub>5</sub>
II <sub>4</sub>	0.180	weak	222	0.181 <sub>5</sub>
			222	0.193
II <sub>5</sub>	0.195	very weak	222	0.193
II <sub>6</sub>	0.209	very weak	124	0.209
II <sub>7</sub>	0.227	very weak	224	0.223
II <sub>8</sub>	0.240	weak	224	0.242
II <sub>9</sub>	0.260	very weak	421	0.264 <sub>5</sub>
			420	0.265 <sub>5</sub>
3. Layer Line				
III <sub>1</sub>	0.194	very weak	130	0.192
			131	0.195
III <sub>2</sub>	0.218	very weak	230	0.217 <sub>5</sub>
			231	0.219
III <sub>3</sub>	0.243	very weak	034	0.242 <sub>5</sub>

2. *Elementary Cell*.—Mark and von Susich found in a more highly oriented preparation that the lattice planes corresponding to the first two equator reflections must be almost exactly perpendicular to each other. In order to be able to classify the interferences which did not conform to the lattices described by them, we attempted to derive an imperfect monoclinic cell, so that both these strong re-

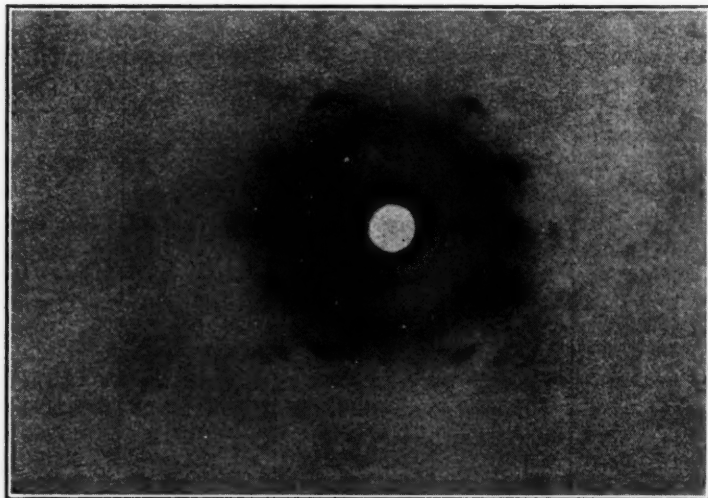


Figure 1—Diagram of Stretched Rubber  
Copper  $K\alpha$  Radiation  
Distance 40.5 mm.

flections could still be explained as half base periods. Various experiments according to the graphic method of Sauter showed that the following monoclinic cell represented all interferences fairly well:

$$\begin{aligned} a &= 8.54 \pm 0.05 \text{ A. U.} \\ b &= 8.20 \pm 0.05^\circ \text{ (fiber axis)} \\ c &= 12.65 \pm 0.05^\circ \text{ A. U.} \\ \sin \beta &= 0.993, \beta = 83^\circ 20' \end{aligned}$$

The angle was so chosen, that the rhombic equator reflection  $A_4$ , which is not indicated, retained its denomination (304).

The  $\sin \theta$  values, calculated from the above axes, are compared with the measurements in Table I. In spite of the reliability of the measurements of the fundamental periods, a number of coincidences occur partly on account of the weakness and lack of sharpness of many interferences, and partly on account of increased possibilities of indications in the monoclinic system. Nevertheless, we believe that the discussion of spatial groups which follows will be adequately supported by the well defined reflections, as well as by the extinctions.

3. *The Number of  $C_6H_5$ -Residues in the Cell*.—The density of stretched crystallized rubber has been measured at various times. In the case of one sample, we were able to confirm the highest value, viz., 0.965, given in the literature.<sup>6</sup> This sample was prepared by evaporation of a benzene solution and was kept in a highly elongated state for 24 hours at  $0^\circ \text{ C.}$  before the measurement was taken. With this value and the volume of  $880^\circ \text{ (A. U.)}$ ,<sup>3</sup> calculated from the cell dimensions,



the number of residues in the cell was found to be  $z=7.6$ . This value lies nearer 8 than the earlier value of 7.1, it is true, but the deviation is still unusually large. Since, however, the same anomaly, although much greater, is also found in the case of the "inorganic rubber," polyphosphornitrile chloride,<sup>7</sup> it may be assumed that it depends on other physical properties of this substance, and results from the loose texture of the extremely small crystallites. The correctness of the density of 1.02, determined from the x-ray diagram of crystallized rubber, in contrast to a value of about 0.94 for amorphous rubber, is also confirmed by the evidence that in the case of other hydrocarbons, namely, paraffins, a variation in density of about 10 per cent has been observed between the solid crystallized state and the liquid, amorphous state (in this connection see the discussion in the paper on inorganic rubber mentioned above).

In any case there does not seem to be any doubt that there are eight  $C_6H_8$  residues in the elementary substance.

4. *Spatial Group*.—The reflections (012) and (304) which are certainly present exclude five groups outright from the thirteen spatial groups of monoclinic systems, so that only the following are left:

$$C_s^1 C_s^2; C_2^1 C_2^2; C_{2h}^1 C_{2h}^2 C_{2h}^4 C_{2h}^5.$$

Of these, three more reflections can be excluded for the following reasons. According to the general physical behavior of rubber (tensile properties), there can be no doubt that long polyprene chains pass through the crystallites in the direction of the fiber axis. The well established chemical formula (see above) shows that such a chain can have no reflecting plane perpendicular to the direction of the chains. Therefore, those spatial groups which have a group of reflecting planes lying perpendicular to the fiber axis in the monoclinic system can be excluded. They are the groups  $C_s$ ,  $C_{2h}^1$ ,  $C_{2h}^2$ . Moreover, the first two of these are very improbable because they do not require any extinction of the odd diatropes.

There remain the groups:

$$C_s^2; C_2^1 C_2^2; C_{2h}^4 C_{2h}^5.$$

Since the extinctions required by the first three groups do not correspond very well to the actual results, we prefer the last two, particularly since the denomination of the general position of the points for the first three of these groups is 2, and for the last two it is 4. A denomination of 2 would indicate that, in the elementary substance, four  $C_6H_8$  residues are crystallographically independent of one another. However, this appears very improbable.

One is probably more justified in choosing between the two remaining groups on the basis of their extinctions. Thus the following systematic extinctions were observed:

$$u00, 0u0, 00u, u0u, g0u \quad (g = \text{even}) \\ (u = \text{odd})$$

Group  $C_{2h}^5$  requires the last four, whereas group  $C_{2h}^4$  requires only the last three; that is, in this case the particularly certain extinction of the odd diatropes would have to take place by means of special layers of the residues, and moreover two adjacent residues of one chain would not be crystallographically equivalent. Both of these suppositions are, however, very improbable.

There is left, therefore, as the most probable spatial group  $C_{2h}^5$ . In this spatial group the observed extinction  $u00$  can be explained by choosing special atomic positions, but it will be seen later that even this may happen without restriction.

The spatial group  $C_{2h}^5$  (Fig. 2) possesses double spiral axes in the direction  $b$ , and sliding reflecting planes in the direction  $c$ , with centers of symmetry between them. (A discussion of the sliding reflecting planes is omitted in what follows, since the spiral axes and centers are sufficiently characteristic in themselves.) The spiral axes are polar, and are connected in pairs by a center of symmetry. Axes 3 and 4 are independent of 1 and 2 crystallographically.

5. *General Consideration of the Chain Structure.*—At the present time the determination of the structure of organic crystals is usually carried out with the aid of the Fourier analysis of intensities introduced by Bragg. This presupposes, however, a general knowledge of the atomic parameter (coördinates in the direction of three axes). If, as is usually the case, with complicated organic structures, all the atoms are in a general position, this determination of the parameter can be solved chiefly only in the presence of sufficiently numerous independent reflections, because the parameters can be determined only from the reflection intensities, and therefore there must be at least as many independent data on the intensities

as there are different parameters to be determined. However, even when this is the case, the problem is not always solvable, since a system of transcendental equations is involved, and these have to be solved graphically.

To establish such a structure without the aid of any hypothesis is practically impossible in the case of highly polymeric organic substances, with their very large elementary cells and relatively poor x-ray diagrams. Moreover, in disregarding the hydrogen atoms, which as a matter of fact, do not contribute noticeably to the scattering, there are in general far more parameters to be determined than the observed reflections.

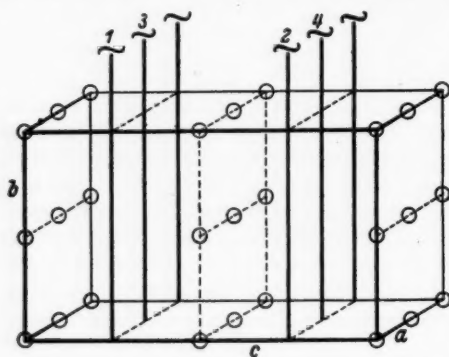


Figure 2—Spatial Group  $C_{2h}^5$ . The Sliding Reflecting Planes in  $\frac{b}{4}$  and  $\frac{3b}{4}$  Parallel to  $ac$  are Omitted  
 T Represents a Double Spiral Axis  
 o Represents a Center of Symmetry

tions. If, therefore, the intensities are to be used primarily for more precise information about the atomic layers, then a discussion of the structure must be based on a molecular model which has been derived from other experimentation. Information on the intensities can then be used in order to verify this model.

Mark and von Susich have developed such a model for rubber. They assumed that all the carbon atoms in a high valence chain lie in one plane. However, this gives a greater length of chain to the  $C_6H_5$  residue than corresponds to one-half the fiber axis, and Mark and von Susich therefore were obliged to kink the chain in the direction of the  $b$ -axis. In this way angles are formed between the valences,

which does not agree with present data, *e. g.*,  $67^\circ$  for the angle  $C \diagup C \diagdown C$ .

Moreover, such a form for the chain would involve, in our spatial group with extinction  $u00$  (see below), another such extinction  $u0g$  as well, which, however, seemed improbable to us because of the presence of (304).

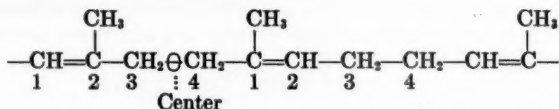
It follows from this, therefore, that the chain is not a plane, but rather a spatial, *i. e.*, three-dimensional, form. However, because of the ability of the simple bonds to rotate freely, this structure is not yet definitely established, even with the

advantage of the fiber periods and the symmetry of the spiral axes (see below), and even with strict retention of the known atomic distances and valence angles.

A chain-like arrangement of the residues in  $C_{2h}^5$  is then possible in two ways:

- The residues are in the vicinity of the centers of symmetry.
- The residues are in the vicinity of the spiral axes, so that the chain is formed by further diagonal coiling of one residue.

The first possibility can be excluded, since the chain formed:



in which the methyl groups are joined alternately to atoms 1 and 2 of a residue, does not agree with the chemical formula which is definitely established by the transformation to levulinic aldehyde by ozonization.

Accordingly there remains, therefore, only the second choice of arrangement, *viz.*, the chains have the symmetry of a double spiral axis, just as in the previous model.

Since one  $C_6H_8$  residue, because of the general position of its atom (not in a plane), has a definite direction of rotation, chains of definite direction of rotation are formed by the spiral axes. In fact, because of the centers of symmetry between the axes, they alternate from stereoisomeric right to left chains. Crystallized rubber represents, therefore, to a certain extent a molecular racemate. Moreover, it is to be assumed that stereoisomerism itself appears only on crystallization. In the amorphous state it is not present on account of the ability of the simple bonds to rotate freely; in the crystallized state it becomes possible because of the fixation of the atoms in the three-dimensional arrangement.

The extinction  $u00$ , which is not required by the spatial group, can be easily explained in the following way.

Since, however, eight  $C_6H_8$  residues are present in the elementary cell, the denomination of the general position of the points is only 4; therefore two residues are crystallographically independent of one another. We can, therefore, bring one near the spiral axis 1 (Fig. 3), and the other near axis 3, so that their projections are reflected in the direction of the fiber axis. If now the chains formed from both residues are given opposite and equal azimuths in relation to the  $c$ -direction, there is extinction  $u00$  as a result of the equal scattering power, without there being at the same time any extinction  $u0g$ . In view of the presence of (304) this is not admissible. The equality of the chain azimuths appears, however, plausible in view of spatial considerations, since in this case chains 3 and 4 have the same relative position as 1 and 2.

The form of the chains based on intensity data will be discussed in greater detail in a later work.

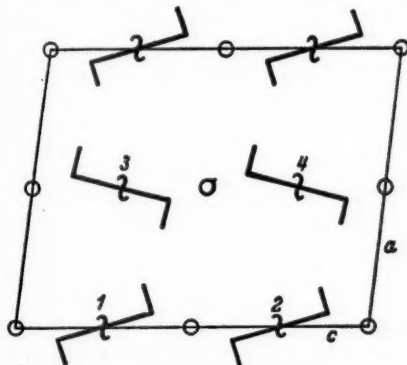


Figure 3—Schematic Arrangement of the Chains in the Cell, with Projections Toward the Fiber Axis

## Résumé

1. The elementary cell of crystallized rubber has been determined anew. It is monoclinic, with axes  $a = 8.57 \pm 0.05$  A. U.,  $b = 8.20 \pm 0.05$  A. U.,  $c = 12.65 \pm 0.05$  A. U.,  $\beta = 82^\circ 20'$ . Four primary valence chains pass through the elementary substance.

2. Statistics of reflections and extinctions as well as chemical considerations make the spatial group  $C_{2h}^5$  appear to be the most probable one.

3. The rubber chains in the crystal have the symmetry of a double spiral axis. The crystallite is a molecular racemate of right and left spiral molecules.

## References

<sup>1</sup> *Naturwissenschaften*, **13**, 410 (1925).

<sup>2</sup> *Kolloidchem. Beih.*, **22**, 64 (1926).

<sup>3</sup> *Kolloid-Z.*, **46**, 11 (1928).

<sup>4</sup> *Ber.*, **61**, 613, 1939 (1928).

<sup>5</sup> Preliminary communication of our results is to be found in the *Compt. rend. soc. phys. Genève*, May, 1936.

<sup>6</sup> Mark and von Susich, see reference 3.

<sup>7</sup> Meyer, Lotmar, and Pankow, *Helv. chim. Acta*, **19**, Oct., 1936.

# An Application of Infrared Spectroscopy to Rubber Chemistry

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In his recent article Barnes<sup>1</sup> has described some of the applications of infrared spectroscopy to problems involving the structure and effective binding forces of complicated organic molecules. The interpretations of the spectra of complex molecules are necessarily empirical but may sometimes be quite valuable to the organic chemist. In the vast amount of work which has been done by workers in infrared and Raman spectra, certain interesting results have been obtained. Thus, for example, one finds such groups as C—H, C—C, and C=C having practically the same oscillation frequencies, regardless of wide variations in the nature of neighboring atoms and atomic groups.

The extension of infrared and Raman methods to the study of highly polymerized materials such as rubber has been limited, even though these methods offer a means of gaining information concerning both the primary chemical linkages and also the forces between units without disturbing either. Spectroscopic studies have been desirable, but until recently experimental difficulties have prevented them. Early attempts to secure a Raman spectrum ended in failure as a result of continuous background radiation, which prevented the observation of distinct Raman lines.<sup>2</sup> This continuous background was attributed by Signer and Weiler to fluorescent end groups or to fluorescent impurities in the samples. More recently Gehman and Osterhof<sup>3</sup> have overcome these difficulties by studying the spectra of rubber in carbon tetrachloride and in carbon disulfide. These investigators were able to secure an excellent Raman spectrum for rubber with the possibility of the obscuration of a few weak lines by fluorescent background and by coincidence with solvent lines.

Even the improved Raman methods leave something to be desired, since results obtained with solutions are never as satisfactory as those obtained with a pure compound. Disturbing effects caused by interactions between solvent and solute are often in evidence. Hence it was decided to attempt the application of infrared methods to this problem. At first glance, it would appear that the difficulties involved in the infrared approach are even greater than in the Raman work. As in the Raman studies one is faced immediately with the problem of a continuous background of apparent absorption, which is actually the result of scattering by surface irregularities and by colloidal particles in the rubber itself. Another difficulty arises in securing appropriate thicknesses for use in absorption measurements. The thicknesses required are in the neighborhood of a few hundredths of a millimeter, thicknesses ordinarily easily obtained with a microtome. However, a microtome cannot be used effectively on a substance having the qualities of rubber. Therefore the absorbing layers employed have to be used in the form in which they were originally deposited.

The spectroscopic methods used have been described in a previous paper.<sup>4</sup> A Hilger infrared spectrometer with a rock salt prism was used as a resolving instrument, and the effective slit-widths were  $0.04\mu$  at  $3\mu$  and  $0.03\mu$  at  $6\mu$ . In order to

have the spectra of simpler compounds of a similar chemical nature available for comparison with the rubber spectrum, the absorption of isoprene and styrene was measured. Isoprene is the unit cell in the highly polymerized rubber complex,

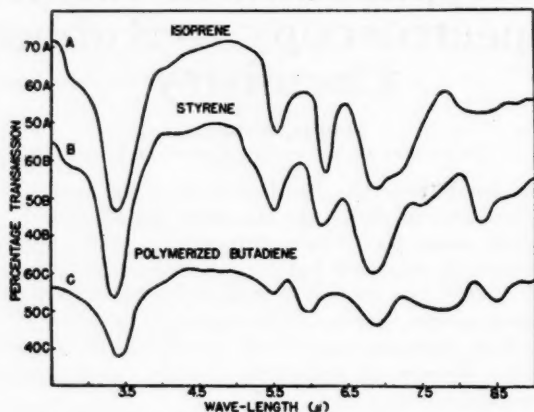


Figure 1—The Percentage Transmission of Isoprene, Styrene, and Polymerized Butadiene. Region:  $2.5\mu$  to  $9.0\mu$ .

and styrene has a number of similar properties. Absorbing layers of these liquids 0.06 mm. in thickness were enclosed in absorption cells equipped with fluorite windows. The other substances studied were natural rubber, vulcanized rubber of low sulfur content, rubber hydrochloride, and polymerized butadiene. The simple

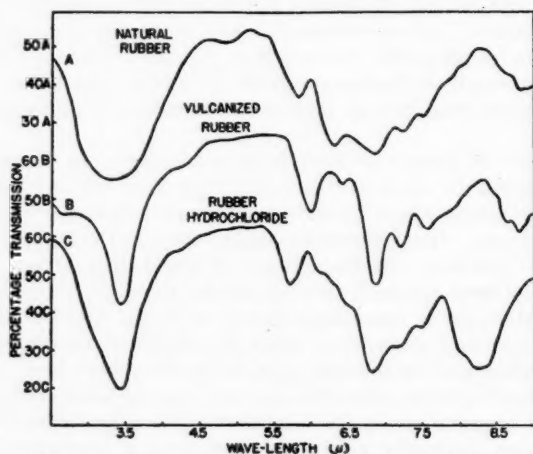
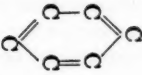
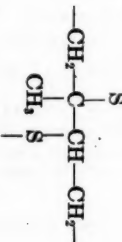
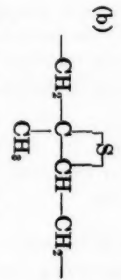
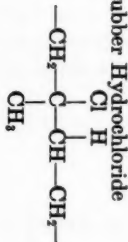


Figure 2—The Percentage Transmission of Natural Rubber, Vulcanized Rubber, and Rubber Hydrochloride. Region:  $2.5\mu$  to  $9.0\mu$ .

gum rubber was prepared from latex in this laboratory, while the vulcanized rubber was a commercial product. The rubber hydrochloride, the isoprene and the styrene were obtained from the Goodyear laboratories. The butadiene polymer was



TABLE I.—FREQUENCIES OF THE OBSERVED ABSORPTION MAXIMA

Chemical Formula	Probable Origin	Characteristic Frequencies
A. Isoprene $\text{CH}_2=\text{C}(\text{CH}_3)-\text{CH}=\text{CH}_2$	$\nu(\text{C}-\text{H})$ $2\nu(\text{C}=\text{C})$ $\nu(\text{C}=\text{C})$ $\delta(\text{CH}_3, \text{CH}_3)$	2985 cm. <sup>-1</sup> 1800 1610 1460 1390 1335 1155 1145
B. Styrene $\text{HC}=\text{CH}_2$ 	$\nu(\text{C}-\text{H})$ $2\nu(\text{C}=\text{C})$ $\nu(\text{C}=\text{C})$ $\delta(\text{CH}_3)$	2995 cm. <sup>-1</sup> 1620 1625 1460 1390 1335 1205 1140
C. Polymerized Butadiene $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-$	$\nu(\text{C}-\text{H})$ $2\nu(\text{C}=\text{C})$ $\nu(\text{C}=\text{C})$ $\delta(\text{CH}_3)$	2920 cm. <sup>-1</sup> 1820 1680 1460 1390 1335 1160 1135
D. Natural Rubber $-\text{CH}_2-\text{C}(\text{CH}_3)=\text{CH}-\text{CH}_2-$	$\nu(\text{C}-\text{H})$ $2\nu(\text{C}=\text{C})$ $\nu(\text{C}=\text{C})$ $\delta(\text{CH}_3, \text{CH}_3)$	2980 cm. <sup>-1</sup> 1725 1600 1460 1390 1335 1160 1135
E. Vulcanized Rubber* (a)  (b) 	$\nu(\text{C}-\text{H})$ $2\nu(\text{C}=\text{C})$ $\nu(\text{C}=\text{C})$ $\delta(\text{CH}_3, \text{CH}_3)$	2900 cm. <sup>-1</sup> 1665 1665 1560 1460 1390 1325 1160 1135
F. Rubber Hydrochloride 	$\nu(\text{C}-\text{H})$ $2\nu(\text{C}=\text{C})$ $\delta(\text{CH}_3, \text{CH}_3)$ $2\nu(\text{C}-\text{Cl})$	2900 cm. <sup>-1</sup> 1755 1460 1390 1335 1210

\* Formulas given by Henne and Shepard, *J. Am. Chem. Soc.*, 56, 1326 (1934).

supplied by H. A. Tanner, and was in the early stages of polymerization. The absorbing layers had the following thicknesses: natural rubber 0.14 mm., vulcanized rubber 0.07 mm., rubber hydrochloride 0.09 mm., butadiene polymer 0.06 mm. The last-named compound had the appearance of a clear, extremely viscous liquid, and the absorbing layer to be studied had to be deposited upon a fluorite plate. Owing to the extreme viscosity of the sample, it was difficult to obtain a smooth layer and considerable scattering took place at the surface.

Figure 1 shows curves representing the percentage transmission of isoprene, styrene, and polymerized butadiene in the region from  $2.5\mu$  to  $9.0\mu$ . It will be noted that the curves show the same general characteristics: intense absorption at  $3.5\mu$  and  $7\mu$ , double absorption maxima in the  $5.5\mu$ – $6.5\mu$  region, and weak bands near  $8.5\mu$ . The bands in the first two curves are sharp and intense, whereas in the curve for polymerized butadiene the absorption maxima are broader and less pronounced. This latter effect is due to scattering by surface irregularities.

Figure 2 shows the percentage transmission of the various types of rubber studied. These curves are very similar to those of Fig. 1 in most ways. However, it will be readily seen that there are radical changes in the region between  $5.5\mu$  and  $6.5\mu$  as compared with the same region in the first figure. Also there are additional minor absorption maxima beyond  $6.5\mu$ . In the curve for rubber hydrochloride there is an intense band at  $8.25\mu$ , which does not appear in the upper curves. Another point of interest is the broadness and lack of sharp definition of the bands in the spectrum of natural rubber, especially in the  $3.5\mu$  region, an effect resulting from the scattering action of colloidal particles since the surfaces of the absorbing layers were quite smooth.

The frequencies of the observed absorption maxima are given in Table I along with a list of the probable origins of the most important frequencies and with the conventional chemical formulas of the compounds. The frequencies given in italic type are the most intense. In attributing the observed absorption to definite oscillation mechanisms the author has been guided by the general rules summarized by Barnes in the article mentioned above. These empirical rules have been developed through the study of data obtained by a number of investigators. Thus one finds the following average values in a number of different compounds:

$\nu(\text{C—H}) \simeq 3000 \text{ cm.}^{-1}$	(1)
$\delta(\text{CH}_2) \simeq 1440 \text{ cm.}^{-1}$	(2)
$\nu(\text{C}=\text{C}) \simeq 1500 \text{ to } 1800 \text{ cm.}^{-1}$	(3)
$\nu(\text{C—C}) \simeq 900 \text{ cm.}^{-1}$	(4)

Barnes gives the value  $1440 \text{ cm.}^{-1}$  only for the deformation frequency of  $\text{CH}_2$ , but in a study of Coblenz' extensive work on organic compounds the author finds that the  $\text{CH}_3$  group has a band in the same region.<sup>5</sup> Also Barnes gives the value for the linear vibration of  $\text{C}=\text{C}$  as  $980 \text{ cm.}^{-1}$  while the author finds the average value to be nearer  $900 \text{ cm.}^{-1}$ . On the basis of these empirical rules the interpretations have been made.

The frequencies of isoprene and natural rubber listed in the table are in agreement with the Raman values obtained by Gehman and Osterhof.<sup>3</sup> These investigators were able to obtain weak Raman lines corresponding to frequencies which were not detected in the present work. The slight differences between the values obtained for the principal frequencies by the different methods may be due to the action of the solvent used in the Raman work. The major difference between the results, however, is the appearance in the infrared spectrum of a band corresponding to a frequency of  $1800 \text{ cm.}^{-1}$ . This band has been classified as the first harmonic of a  $\text{C}=\text{C}$  vibrational frequency, but this harmonic frequency evidently does not give rise to a

Raman line. It will be noted that intense bands appear in the vulcanized rubber and the rubber hydrochloride spectra at  $1665\text{ cm.}^{-1}$  and  $1755\text{ cm.}^{-1}$ , respectively. Since most of the double bonds have been broken, these bands have likewise been attributed to the first harmonic of a C—C vibration, the frequency of the vibration having been decreased by the heavy sulfur and chlorine atoms present. The band appearing at  $1210\text{ cm.}^{-1}$  in the spectrum of rubber hydrochloride probably arises from a vibration in which a chlorine atom is involved, as an intense band of this frequency does not appear in the spectra of the other compounds studied. As mentioned above, the sulfur content of the sample of vulcanized rubber is low, and hence some double bonds remain unbroken. The weak band corresponding to a frequency of  $1560\text{ cm.}^{-1}$  may be due to a C=C vibration having a frequency lower than the usual value as a result of heavy neighboring units.

It has been the purpose of the writer to demonstrate the applicability of infrared technic to the problems of rubber chemistry, rather than to obtain data on samples of extreme purity. The results seem to indicate that valuable information can be gained by infrared methods. The measurements made with a prism spectrometer do not show the presence of all the minor frequencies obtained in Raman work, but the necessity for a solvent with all its disturbing effects is removed. It should prove interesting to observe the effects of stretching on the absorption spectrum of rubber, since it has been shown<sup>6</sup> that the mechanism of elastic stretch is intimately connected with the structure of the rubber molecule itself. The effects of various degrees of vulcanization can likewise be readily determined by infrared methods.

The author wishes to acknowledge his indebtedness to Professor E. K. Plyler of the University of North Carolina for the use of his laboratory facilities and to Professor Edward Mack, Jr., and H. A. Tanner for supplying certain of the samples studied and for offering many helpful suggestions.

### References

- <sup>1</sup> Barnes, *Rev. Sci. Inst.*, **7**, 265 (1936).
- <sup>2</sup> Signer and Weiler, *Helv. Chim. Acta*, **15**, 649 (1932); Franklin and Laird, *Phys. Rev.*, **36**, 147 (1930); Busse, *J. Phys. Chem.*, **36**, 2862 (1932); Gehman, *J. Am. Chem. Soc.*, **57**, 1382 (1935).
- <sup>3</sup> Gehman and Osterhof, *J. Am. Chem. Soc.*, **58**, 217 (1936).
- <sup>4</sup> Gordy and Williams, *J. Chem. Phys.*, **3**, 664 (1935).
- <sup>5</sup> Coblenz, Carnegie Inst. of Wash. Pub. No. 35 (1905).
- <sup>6</sup> Mack, *J. Am. Chem. Soc.*, **56**, 2757 (1934).

## Concerning the Alleged Absorption of Gaseous Nitrogen by Benzene Solutions of Rubber and Gutta-Percha Hydrocarbons

Louis B. Howard<sup>1</sup> and Guido E. Hilbert

Experiments described by de Jong<sup>2</sup> have been interpreted as indicating that dilute benzene solutions of rubber or gutta-percha hydrocarbon from sheet balata, when exposed to sunlight for a few days in either quartz or ordinary glass vessels, absorb gaseous nitrogen in appreciable amounts.<sup>3</sup> If such a photochemical combination of rubber and nitrogen actually occurs, one might reasonably expect other unsaturated hydrocarbons containing isoprene units such as carotene and xanthophyll to behave similarly. These substances which always are found closely associated with chlorophyll in green plants possess physiological functions which, as yet, remain quite obscure. It therefore seemed of very great importance from both a theoretical and a practical standpoint to attempt to confirm these results of de Jong.

In the present study the experimental procedure of the original investigation was followed as closely as the description of the work allowed. Several variable factors, such as temperature, barometric pressure, vapor pressure of the benzene solutions, and the heating effect of sealing the tubes, were controlled. In one experiment Pyrex tubes of 150-cc. capacity were filled with 100 cc. of nitrogen gas and 50 cc. of benzene solutions containing about 0.5% of either pale crepe rubber or balata. After sealing, these tubes and a benzene control were exposed to direct sunlight during the summer for various lengths of time up to five weeks. At the end of the tests the changes in volume of the nitrogen in the tubes containing the rubber solutions differed from that of the benzene control by a maximum of 0.5 cc. which was found to be about the limit of experimental error.

Another series of experiments was carried out in an apparatus which consisted of several volumetric reaction chambers in the form of glass tubes fitted with stop-cocks and attached to a mercury leveling bulb. The tubes were charged with about 100 cc. of nitrogen and one, reserved for a control, with 50 cc. of pure benzene and the others with 50 cc. each of 1.1% benzene solutions of one of the following types of rubber: pale crepe (from a shipment just received), fine Para from South America, smoked sheet, or balata. Even though the tubes were exposed to direct sunlight for three months during the summer the slight changes in volume of the gas were in every case less than 1 cc. and, in each of the rubber solutions, were actual increases.

It may be concluded that under the conditions described and with the specimens of rubber, nitrogen, and benzene used, nitrogen gas is not absorbed to any appreciable extent.

### References

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<sup>2</sup> de Jong, *Rec. trav. chim.*, **51**, 153 (1931).

<sup>3</sup> In one case a tube containing 54 cc. of a 1.05% solution of rubber in benzene under an atmosphere of nitrogen was found to draw in 11 cc. of water when opened under the surface of this liquid after six days of irradiation. This was considered to indicate an absorption of 12.8 mg. of nitrogen which according to his calculations represented 2.5% of the weight of the rubber.

# Chemistry of Soft Rubber Vulcanization

## V. Treatment of Dilute Rubber Cements with Sulfur Chloride

B. S. Garvey, Jr.

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**P**REVIOUS investigations (5, 6, 7, 8) indicated that vulcanization of rubber involves the establishment of a mechanical structure in the mass. This structure is apparently produced by changes in the hydrocarbon brought about by two chemical reactions: (a) addition of the vulcanizing agent and (b) a reaction of the hydrocarbon catalyzed by the vulcanizing agent.

The experiments reported in this paper are concerned with the effect of sulfur chloride on the viscosity of dilute rubber cements under various conditions and with the solubilities of films obtained by evaporating cements treated with sulfur chloride. Consideration of the results has suggested a new interpretation of the nature of vulcanization.

Experiments of a somewhat similar type have been reported by Bernstein (1, 2, 3), Fromandi (4), Kirchhof (10, 11), LeBlanc and Kröger (12, 13), Porritt (16), and Weber (18). In most of their investigations they used 100 per cent by weight of sulfur monochloride on the rubber. Since ordinary cold-cured articles contain about 1 per cent of sulfur monochloride, the effect of this small amount is most significant.

### Expressions and General Procedure

Certain expressions used in this paper are defined in terms of the experimental details.

The rubber used was first latex crepe.

One-pass rubber is rubber which has been passed once through a tight mill. This one pass is necessary because sheets of crepe do not always make smooth cements.

Masticated rubber is rubber which has been milled for 20 minutes on an 8-inch mill in 400-gram batches. In Table I other degrees of mastication are specified.

Cement is the solution of rubber in benzene which has been dried over calcium chloride. The concentration is given as per cent of rubber by weight. Thus a 1 per cent cement contains 1 gram of rubber in 100 grams of cement.

Concentration refers to the concentration of rubber in the cement and is expressed as per cent by weight.

Per cent sulfur monochloride is based on the weight of the rubber. Thus the addition of 1 per cent sulfur monochloride means the addition of a weight of sulfur monochloride equal to 1 per cent of the rubber in the cement. The sulfur monochloride was added as a benzene solution.

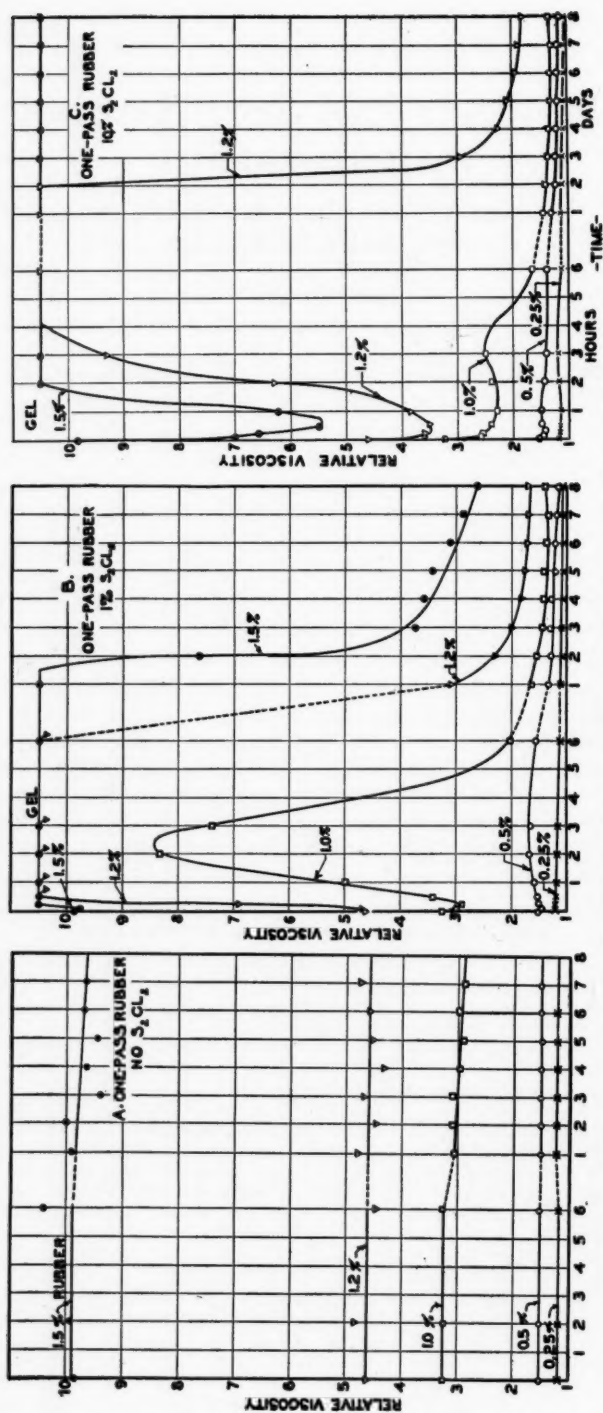


FIGURE 1. EFFECT OF SULFUR MONOCHLORIDE ADDITION ON VISCOSITY OF CEMENTS FROM ONE-PASS RUBBER



Viscosity is the relative viscosity where:

$$\text{relative viscosity} = \frac{\text{time of flow of cement, seconds}}{\text{time of flow of benzene, seconds}}$$

Viscosities were determined in a Saybolt viscometer.

Gel refers to the formation of a gel in the cement. Viscosities could not be determined for gelled cements. In the curves the times at which the cements were gelled are shown by the points on the line marked "Gel" at the top.

Unless otherwise stated, the work was done in the diffused daylight of the laboratory, care being taken to prevent direct exposure to windows, and at room temperature usually between 20° and 25° C.

Exact duplication of results with different cements was almost impossible. However, when comparative experiments were run with series of cements of different concentrations, the same trend could be observed in each series. The experiments reported are typical of the large number which were performed.

### Effect of Sulfur Chloride on Viscosity

Figures 1 and 2 show how the viscosity changed with time after the addition of sulfur chloride to cements of one-pass rubber and of masticated rubber of different concentrations. For this whole series the conditions of light and temperature were nearly the same. The cements were exposed to diffused daylight during the addition of sulfur chloride and during the actual viscosity measurements. The rest of the time they were kept in a dark cupboard at room temperature.

In the absence of sulfur chloride the viscosities of the cements remained practically unchanged for the full time of the experiments (Figures 1A and 2A).

Pronounced differences were apparent between the cements made from one-pass rubber and those made from masticated rubber, not only in the viscosity of the original cements but also in the viscosity changes after the addition of sulfur monochloride. The well-known difference in viscosity between cements of the same concentration but with rubber of different degrees of mastication can be seen by comparing Figure 1A with 2A. A comparison of Figures 2B and C with 1B and C shows that cements of masticated rubber required considerably higher concentrations of rubber in order for the sulfur monochloride to cause any significant change in viscosity than did cements of one-pass rubber. The change in viscosity with time after the addition of sulfur monochloride was also different for the two kinds of rubber as can be seen by comparing the curves of Figures 1B and C with those of Figure 2B and C.

In many cases a rise in viscosity was followed by a fall in viscosity—i. e., a reversion (Figures 1B and C, and 2B). The 0.25 per cent cement of one-pass rubber showed a slight drop in viscosity which was not preceded by any significant rise (Figures 1B and C).

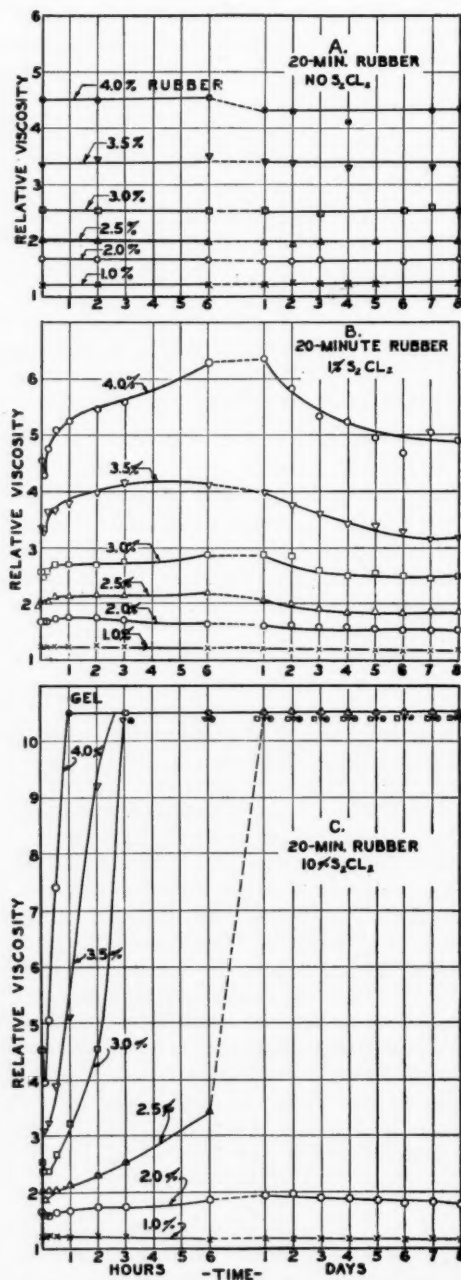


FIGURE 2. EFFECT OF SULFUR MONOCHLORIDE ADDITION ON VISCOSITY OF CEMENTS FROM MASTICATED RUBBER

After reversion the viscosities of both types of cement approached that of a cement of masticated rubber which had the same concentration but had not been treated with sulfur monochloride. In the case of masticated rubber this means that the final viscosity was nearly the same as the initial viscosity (the 3.5 per cent cement in Figure 2*B*). In the case of one-pass rubber, on the other hand, it means that the final viscosity was much lower than the initial viscosity, as shown by comparing the final viscosity of the 1 per cent cement in Figures 1*B* and *C* with its initial viscosity and also with the initial viscosity of the 1 per cent cement in Figure 2*A*.

A comparison of the viscosity changes following the addition of increasing amounts of sulfur chloride shows a striking difference. For masticated rubber the effect of 10 per cent sulfur monochloride as compared with 1 per cent was approximately what might have been expected according to the law of mass action; i. e., the higher percentage of sulfur monochloride caused the greater and the faster increase in viscosity, especially with the more concentrated cements (Figures 2*B* and *C*). For one-pass rubber, however, this was not the case. The 1 per cent cement, in particular, showed a much greater increase in viscosity when treated with 1 per cent sulfur monochloride than when treated with 10 per cent (Figures 1*B* and *C*). It was frequently the case that a cement could be made to gel quickly with 1 per cent of sulfur monochloride and not at all with 10 per cent. This result was confirmed by repeated experiments with cements of one-pass rubber at concentrations between 0.8 and 1.0 per cent. Obviously gel formation did not always follow the law of mass action.

Gel formation did not parallel either the concentration of the cements (as shown by comparing the 1.5 per cent cement in Figure 1*B* and the 2.0 per cent in Figure 2*B*) or their viscosities (the 1.2 per cent cement in Figure 1*B* and the 4 per cent cement in Figure 2*B*). However, viscosity varies not only with the concentration but also with the mastication of the rubber. Numerous experiments showed that where the viscosities of a series of cements could be taken as a measure of the concentration of the rubber or the extent of its mastication, the cements of higher viscosity were more likely to gel than those of lower viscosity. Thus there is suggested some sort of relation between gel formation and the proximity of the individual molecules to one another in the cement.

### **Effect of Light and Temperature on Viscosity Changes**

Certain anomalies which appeared from time to time, when the experimental conditions were not so closely comparable as those for the previous experiments, seemed to be caused

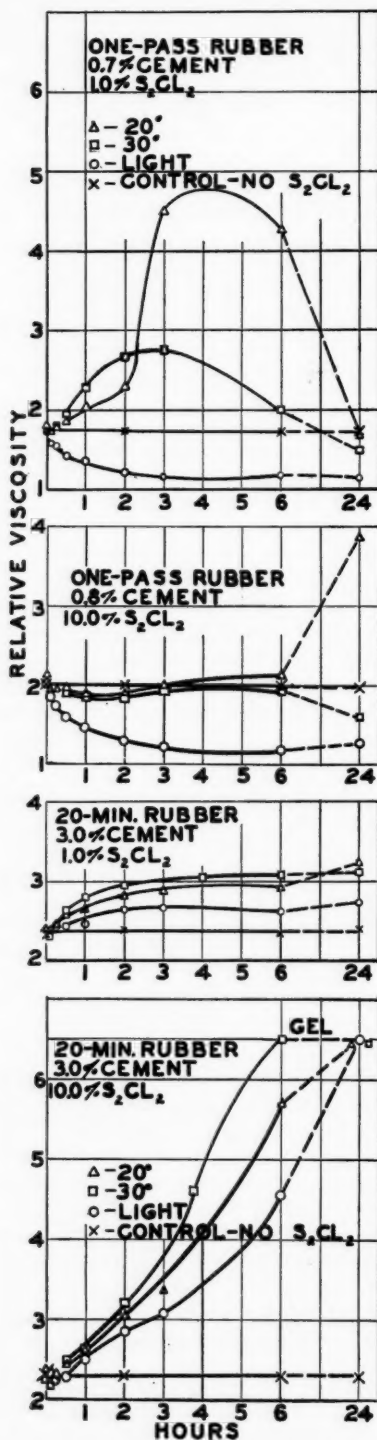


FIGURE 3. EFFECT OF LIGHT AND TEMPERATURE ON VISCOSITY CHANGES OF RUBBER CEMENTS

by changes in temperature or light intensity. Figure 3 gives typical curves illustrating the effect of these two factors.

The data for these curves were obtained as follows:

A. The cements were kept in black flasks (painted on the outside with a heavy graphite paint) in a thermostat at 20° C. and viscosities were determined at 20° over the first 6 hours. They were then allowed to stand overnight at room temperature (about 25° C.) and the viscosities were again determined at 20° C.

B. The cements were handled as in A except that the thermostat was kept at 30° C. and viscosities were determined at 30° C.

C. The cements were kept in clear Pyrex glass flasks at room temperature (25° to 30° C.) and were exposed to diffused daylight on clear days in December and January. They were protected from any exposure to direct sunlight. Viscosities were determined at room temperature.

D. The cement was treated as in C except that no sulfur monochloride was added. Similar controls were run in black flasks at 20° and 30° C., but the three curves so nearly coincided that only one is given.

Light of the intensity prevailing in these experiments had no effect on the viscosity in the absence of sulfur monochloride. It did, however, have a distinct effect in preventing or slowing the rise in viscosity caused by sulfur monochloride. This effect is most pronounced with one-pass rubber and 1 per cent of sulfur monochloride where the viscosity rose in the dark but fell in the light. Other experiments showed that direct sunlight frequently prevents gel formation and disperses many gels.

At 30° C. the viscosity change caused by sulfur chloride takes place somewhat more rapidly than at 20°. With one-pass rubber and 1 per cent of sulfur monochloride the rise in viscosity is not so great and the subsequent drop is faster. Other experiments showed that raising the temperature raised somewhat the concentration required for gel formation. At higher temperatures, the gels were softer and reverted more quickly to ungelled cements. Similar effects of temperature were observed by LeBlanc and Kröger (13), using larger amounts of sulfur monochloride.

### Solubility of Films

Interesting observations were made on the solubility of the films obtained by evaporating cements treated with sulfur chloride. While all of the gelled cements gave insoluble films, those which were not gelled sometimes gave soluble and sometimes insoluble films.

On investigation it was found that, if a cement, which did not gel after treatment with sulfur monochloride, was evaporated within 6 hours after the sulfur monochloride was added, the resulting film was not readily soluble. If, however, the cement was allowed to stand for several days before evaporation, the resulting film was readily soluble. The length of time required to give a soluble film before evaporation

was found to decrease with the mastication of the rubber and to increase with the concentration of the cement and the amount of sulfur monochloride added. The data are summarized in Table I.

The following procedure was used in obtaining the data for Table I:

The volume of cements was adjusted so that each contained the same amount of rubber: 33 cc. of 3 per cent cement, 67 cc. of 1.5 per cent cement, 100 cc. of 1 per cent cement, and 200 cc. of 0.5 per cent cement. The designated amount of sulfur monochloride was added as a benzene solution. After standing for the designated length of time in a dark cupboard, the cements were evaporated by blowing a slow stream of air through the flasks for 24 hours. To each film were then added 200 cc. of benzene. The samples designated "easily soluble" dissolved completely in 24 hours without stirring. Those designated "soluble" dissolved in 24 to 48 hours if stirred occasionally with a rod. Those were said to be "grainy" in which the film swelled

TABLE I. SOLUBILITY<sup>a</sup> OF FILMS FROM CEMENTS TREATED WITH SULFUR MONOCHLORIDE

Rubber	Cement, %	Time of Standing			
		6 hr.	24 hr.	10 days	10 days
		Amount of $S_2Cl_2$			
		1%	1%	1%	10% <sup>b</sup>
1-pass	3.0	1	1	1	1
	1.5	1	1	2	1
	1.0	1	1	4	1
	0.5	1	1	4	1
5-pass	3.0	1	1	1	1
	1.5	1	1	3	1
	1.0	1	1	4	1
	0.5	1	1	4	1
10-pass	3.0	1	1	4	1
	1.5	1	2	4	1
	1.0	1	2	4	2
	0.5	1	4	4	4
20-min.	3.0	2	4	4	1
	1.5	2	4	4	2
	1.0	2	4	4	3
	0.5	2	4	4	4

<sup>a</sup> 1 = swollen; 2 = grainy; 3 = soluble; 4 = easily soluble.

<sup>b</sup> With 10%  $S_2Cl_2$  the cements after 6- and 24-hour standing gave swollen films.

to a gel that was broken to a grainy consistency when stirred with a rod. Those designated "swollen" remained as a firm, swollen film even after 48 hours with occasional stirring with a rod.

### Effect of Mechanical Agitation

If mechanical bonding plays an important part in vulcanization, it might be expected that mechanical agitation of the cements after the addition of sulfur monochloride would have a pronounced effect on the viscosity changes and gel formation. In fact, it was found that mechanical agitation not only prevented gel formation in many cases but also increased the solubility of the films obtained by evaporation of cements.



Cements in wide-mouth Erlenmeyer flasks were agitated by glass propellers. In the absence of sulfur chloride this agitation had little or no effect on the viscosities of the cements. The same results were observed when the agitation was carried out in atmospheres of air, nitrogen, or carbon dioxide, showing that, if oxygen affected the results, only traces were required.

The most pronounced effects were observed with one-pass rubber and 1 per cent of sulfur monochloride on the rubber. At rubber concentrations of about 1 per cent, cements in which gels had formed quickly without agitation gave no sign of gel formation when stirred. At rubber concentrations of about 1.5 per cent, the cements soon thickened and piled around the stirrer. On continued agitation they again became thin and after 6 to 12 hours were smooth and of much lower viscosity than before treatment.

With cements of masticated rubber the effect of agitation was less pronounced. In several cases where 10 per cent of sulfur monochloride was used, the cements did not gel while being agitated, but did within a few hours after agitation was stopped.

The effect of agitation of the cement on the solubility of the film is shown by the following experiment: Four samples of a 1 per cent cement of one-pass rubber were treated with 1 per cent sulfur chloride. Those not agitated were kept beside the others and treated the same way except for stirring. The 6-hour sample was stirred continuously after the addition of the sulfur monochloride. The 24-hour sample was stirred 12 hours, allowed to stand 12 hours, and finally stirred for 10 minutes. The cements were evaporated as described previously. To each film were added 200 cc. of benzene. After 24 hours all gave swollen films which were stirred for 2 hours. At the beginning it was necessary to start and stop the stirrers several times before they would stir smoothly. The cements were then filtered through cheese-cloth. The proportion of dissolved material was as follows:

Time of Standing or Agitation, Hr.	Per Cent Dissolved	
	Agitated	Not agitated
6	80	55
24	100	75

### Relation between Viscosity and Solubility

It is interesting to compare the viscosity of the cement and the solubility of the film for two samples of the same cement of one-pass rubber; sample *A* was not treated with sulfur monochloride, and sample *B* was treated with 1 per cent sulfur monochloride with agitation. *A* is the more viscous cement and gives the more soluble film. If the less soluble film is dissolved with the help of agitation, the resulting cement is less viscous than that from the more easily soluble film.

### Discussion of Results

In these experiments no attempt was made to exclude oxygen. However, all conclusions are based on comparative experiments and any effect of oxygen would have to be due to a difference in its action when sulfur monochloride was present and when it was absent. If there is such a differential action, it must be a common factor in technical and experimental curing operations.

A study of these experiments has suggested some new

ideas on the nature of vulcanization. In the following discussion these ideas are advanced as working hypotheses.

### **Mechanical Nature of Vulcanized Structure**

Apparently sulfur monochloride changes the individual molecules, but a vulcanized structure can be established only if the molecules are close enough together. Thus the insolubility of the films from ungelled cements treated with sulfur monochloride indicates that a change has occurred in the individual molecules. The vulcanized structure, however, is not apparent in the cement where the molecules are isolated, although it is manifest in the film where they are packed together. Likewise the apparent relation between gel formation and the proximity of the individual molecules to one another suggests that, when the molecules are far enough apart, a vulcanized structure cannot be established. The effect of agitation on gel formation and on the solubility of the films points to the mechanical nature of this structure.

### **Reversion of Vulcanized Structure**

A reversion or disintegration of the vulcanized structure is indicated by the drop in viscosity following the initial rise due to its formation. The increase in solubility of the film after the cements have been allowed to stand is evidence that this reversion may be due to changes in the individual molecules, which can take place fairly quickly in dilute solution.

### **Crude Rubber Structure**

Evidence that in crude rubber there is a structure which is broken down by mastication is found in the difference in viscosity between cements of masticated and unmasticated rubber, in the differences in viscosity change after the addition of sulfur monochloride, and in the differences between the two types of cement with regard to gel formation and film solubility.

This crude rubber structure is apparently lost during the formation and disintegration of the vulcanized structure since the viscosity of a reverted cement of one-pass rubber is close to that of an untreated cement of masticated rubber of the same concentration. The viscosity of a reverted cement of masticated rubber is nearly that of the original cement.

### **Catalyzed Reaction**

If the insolubility of the films obtained by evaporation of the treated cements were due to sulfur monochloride bridges (2, 9, 15, 18) between double bonds, we would not expect to increase the solubility of the film by allowing the cements to stand before evaporation. The discrepancy between gel formation and the law of mass action also suggests that sulfur monochloride acts in some manner other than by direct addition to double bonds.

A clue to the nature of this action is that many thin cements which had been treated with sulfur monochloride yielded insoluble films whereas much more viscous cements which had not been so treated yielded films which were readily soluble. The insolubility of the films appears to be due to the mechanical interlocking of the molecules as the solution is evaporated—a sort of "molecular felting." Since unvulcanized rubber does not show this felting, the reaction must change the molecule in such a way that it can felt. If the rubber molecules are long and comparatively straight fibers they would not be expected to show much felting action.

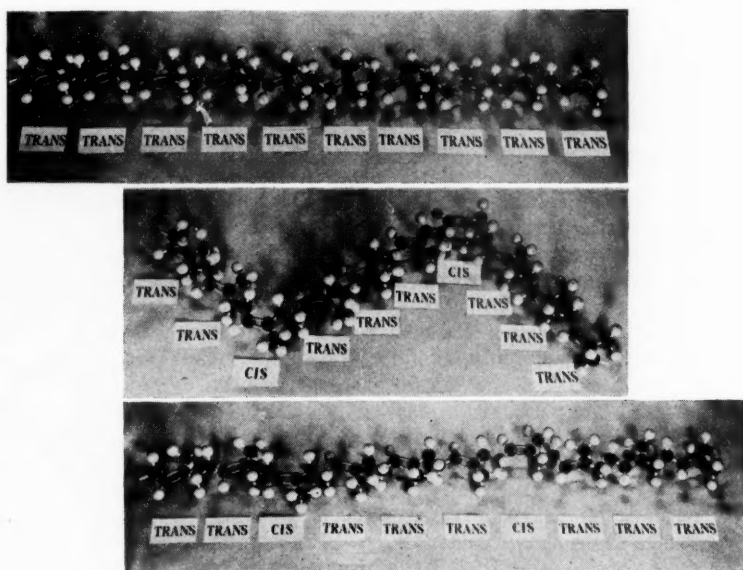


FIGURE 4. EFFECT OF SULFUR MONOCHLORIDE ON MOLECULAR ARRANGEMENT

If, however, they were bent in a number of places so as to become kinky, they should felt. For example, a mass of straight wires is readily untangled, but untangling a mass of bent kinky wires is difficult. These experiments suggest, therefore, that sulfur monochloride makes the comparatively straight-fiber molecules of crude rubber become kinky.

Since allowing the cements to stand increases the solubility of the films obtained from them, it follows that the kinkiness is lost under these conditions. In dilute solutions where the molecules are isolated from one another, they straighten out quickly, suggesting that mechanical entanglement in the cement may slow up the straightening of the molecules. This suggestion is strengthened by the fact that mechanical agitation increases the solubility.

One explanation of the chemistry involved is that sulfur

monochloride causes geometrical rearrangement at some of the double bonds similar to the rearrangement of oleic acid into elaidic acid brought about by sulfur (17). If, in a straight molecule with all of the double bonds in the *trans* form as shown in the upper photograph of Figure 4, rearrangement takes place at some of the double bonds, the molecule would become kinky as shown in the center photograph. By free rotation around single bonds under the influence of thermal agitation, this kinky molecule could again become comparatively straight as shown in the lower photograph of Figure 4, provided there is any tendency for the polyolefin molecules to form an extended straight chain.

According to this hypothesis the catalyzed reaction causes vulcanization by "mechanical cross bonds" formed by the interlocking of the molecules as they become kinked. The chemical addition of the sulfur monochloride to the hydrocarbon apparently forms sulfur monochloride bridges between fiber molecules (2, 4, 15, 18)—i. e., "chemical cross bonds." The product would contain both types of cross bonds in numbers depending on the extent to which the two reactions had taken place. In addition, the effect of the mechanical bonds would be different if established before the chemical bonds rather than afterwards. Thus the final vulcanized structure and the physical properties of the vulcanizate would depend on the extent and relative rates of the two reactions establishing the two types of cross bonds.

The possibility that geometric rearrangement may play an important part in vulcanization has hitherto been generally disregarded. The only references are those of Lindmayer (14) who, after pointing out some of its possibilities, adopted an entirely different explanation of vulcanization. This hypothesis of geometric rearrangement fits well with many known facts about vulcanization. Its relation to types of vulcanization other than that with sulfur monochloride seems worthy of consideration.

### Literature Cited

- (1) Bernstein, G., *India Rubber J.*, **48**, 164, 522 (1914).
- (2) Bernstein, G., *Kolloid-Z.*, **11**, 185 (1912).
- (3) *Ibid.*, **12**, 193, 273 (1913).
- (4) Fromandi, G., *Rubber Chem. Tech.*, **4**, 8 (1931).
- (5) Garvey, B. S., Jr., *Ind. Eng. Chem.*, **26**, 434 (1934).
- (6) *Ibid.*, **26**, 437 (1934).
- (7) Garvey, B. S., Jr., and Thompson, G., *Ibid.*, **25**, 1292 (1933).
- (8) Garvey, B. S., Jr., and White, W. D., *Ibid.*, **25**, 1042 (1933).
- (9) Hinrichsen, F. W., and Kindschor, E., *Kolloid-Z.*, **6**, 202 (1910).
- (10) Kirchhof, F., *Kautschuk*, 1927, 28.
- (11) Kirchhof, F., *Kolloid-Z.*, **14**, 35 (1914).
- (12) LeBlanc, M., and Kröger, M., *Kolloid-Z.*, **33**, 168 (1923).
- (13) LeBlanc, M., and Kröger, M., *Z. Elektrochem.*, **27**, 335 (1921).
- (14) Lindmayer, E., *India Rubber J.*, **82**, 218, 249 (1931).
- (15) Meyer, K. H., and Mark, H., *Ber.*, **61**, 1939 (1928).
- (16) Porritt, B. D., *India Rubber J.*, **60**, 1159 (1920).
- (17) Rankoff, G., *Ber.*, **64B**, 619 (1931).
- (18) Weber, C. O., *J. Soc. Chem. Ind.*, **13**, 11 (1894); "Chemistry of India Rubber," pp. 97 et seq., London, Griffin & Co., 1909.

# A Survey of Latex Coagulants Used by Malayan Small-Holders

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Although rubber produced on small holdings has for many years formed a large part of the total amount of rubber exported from Malaya, it has not until recently become possible to obtain reliable information as to the nature of the coagulants commonly used by small producers. A great part of the rubber from Malayan small holdings finds its way to the United States of America and, although a steady demand might perhaps be taken as some indication that the intrinsic properties of such rubber are reasonably satisfactory and dangerous coagulant substances are therefore not in general use, it was nevertheless considered necessary to take the first opportunity of making a survey of coagulants commonly employed. Information based on direct analyses of reliable samples drawn from all parts of the country has been lacking and, in its absence, nobody could state with any certainty that the most suitable available coagulants were used either universally or even by the majority of small holders. A survey of this nature demands for its prosecution an organization which is able to make a close search through many villages in all districts, because most small holders, or the tappers employed by them, purchase their supplies of coagulant in small bottles from local shops and there can be no certainty that the coagulants sold in one shop are identical with those sold in others nearby, or in neighboring villages. The recent establishment of the Small-Holders' Advisory Service with Asiatic Rubber Instructors stationed in a number of districts made such a survey possible and towards the end of 1934 coagulants were collected in the States of Kedah, Perak, Negri Sembilan, Pahang, Selangor, Johore, and also in Malacca Territory.

## Sampling and Testing

The Asiatic Rubber Instructors who were responsible for the collection of samples purchased unopened bottles of all available brands of coagulant from shopkeepers in all districts. Their meetings with the small holders also often enabled them to discover which brands if any were specially favored in the district. The samples were forwarded to the Institute for analysis, with notes as to cost and, where possible, relative popularity.

Before analysis, the volume of each sample was measured so that, where analysis indicated that components were present in a diluted form, fairly accurate cost comparisons could be made against the price of the same material at commercial strength.

Each sample was analyzed qualitatively and the amounts of major and minor components were determined. No attempt was made, however, to estimate the amounts of harmless impurities of which traces were found in some samples. Careful watch was kept for traces of the metals, copper and manganese, but in no case were they found present in dangerous amounts.

The results of the analyses of samples collected and tested between September, 1934, and March, 1936, are set out and discussed according to States.



### Coagulants Used by Small Holders

*The State of Kedah.*—In addition to sulfuric acid, formic acid, acetic acid, and hydrochloric acid, a few small holders were found to be employing alum as a coagulant and, in rarer cases, sodium bisulfite. The survey indicates that of the twenty-eight different brands of coagulant used in this State, sixteen contained sulfuric acid alone, or were mixtures in which it was either a major or a very appreciable component. In eight of these cases sulfuric acid was the only coagulant present; in five cases it appeared in admixture with small amounts of hydrochloric acid, and in three other instances it was found in association with alum, acetic acid, and formic acid, respectively. The concentration of sulfuric acid varied approximately between 22 and 67 per cent from brand to brand. This is indicative of considerable dilution by the bottlers, who are no doubt actuated firstly, by considerations of profit; secondly, by the possible loss of trade which might result from injuries by a 95 per cent commercial acid in the hands of unskilled persons; and thirdly, by the desire to offer a product which, although cheaper to produce will have approximately the same efficiency as formic or acetic acid of good quality.

Six samples were formic acid of good quality of which the strengths lay between 79 and 90 per cent. This acid is sold commercially in two strengths of 80 per cent and 90 per cent, so that a charge of dilution by the bottler cannot here be made with fairness. Four samples were undiluted acetic acid of good quality.

*The State of Perak.*—The situation in Perak is very similar to that in Kedah. Of forty-four samples analyzed, no fewer than twenty-seven consisted either of sulfuric acid alone or contained it as a very appreciable component. Mixtures of sulfuric acid with alum, hydrochloric acid, acetic acid, or formic acid were again found. The concentration of sulfuric acid from brand to brand varied over the range 22–69 per cent, which is similar to that found for preparations used in Kedah. Many of the brands used in Kedah are also found in Perak and emanate from the same group of wholesale bottlers. Of the seventeen samples of formic acid found in this State, eight were in use in the single district of Selama. Six of the samples of formic acid were seriously below commercial strength and had obviously been diluted deliberately by the bottler. No samples were found in which acetic acid was the sole coagulant present.

Reports from the various districts indicated that the more popular brands were those which were later found to consist either solely or mainly of sulfuric acid.

*The State of Negri Sembilan.*—The investigations made in this State indicated beyond doubt that the coagulant in almost exclusive use is formic acid of good quality and strength. One sample, though labeled "acetic acid," was found to consist of 88.2 per cent formic acid. The survey revealed only one sample consisting of any coagulant other than formic acid. This sample was "Aeroplane Brand" coagulant (see Perak No. 3) containing 57 per cent of sulfuric acid. In this State, however, this brand of coagulant was not found to be popular, and the conclusion can safely be drawn that formic acid is the coagulant in general use.

*The State of Pahang.*—In this State, formic and acetic acids are used exclusively. Of twenty-five samples, twenty were found to consist of formic acid and five of acetic acid. In four instances formic acid was being sold in a diluted condition but, in all other cases, the coagulant, whether formic or acetic acid, was of reasonably good commercial strength.

*The State of Selangor.*—The search in this State revealed that formic and acetic acids are used almost exclusively. In all, five samples consisting of sulfuric acid were found, and these represented in each case the remains of consignments which had proved to be virtually unsalable in the various districts. Of these, four were



brands which find a ready sale in the north but the Selangor small holders are not apparently converted to their use. In the remaining instance, 34.5 per cent sulfuric acid was being offered as acetic acid, but it was not popular. It is fairly common practice in some parts of this State for the head man of a village to purchase a whole demijohn of commercial formic acid and to issue it in small lots to the small holders. It may be said of this State that undesirable coagulants are not in use.

*The State of Johore.*—In addition to formic acid, sulfuric acid, and hydrochloric acid, a number of small holders were employing self-made mixtures of alum with acid. It will be observed that, in this State, formic and acetic acids are not used exclusively, and in North Johore one of the two brands most popular with small holders contains a by no means negligible proportion of sulfuric acid. Four other brands of coagulant containing this acid either alone or in appreciable proportions were finding a sale in various districts and, in view of these facts, it would appear that in this State the amount of rubber produced by the use of sulfuric acid cannot be taken as negligible.

*Malacca Territory.*—In this territory formic and acetic acids are seen to be in exclusive use, but in two cases formic acid was being sold in a diluted condition.

#### **Bottling of Coagulants**

In nearly all cases, the samples consisting essentially of sulfuric acid were being sold in bottles bearing colored distinctive labels designed to attract the eye. In most cases the label gave no indication of the chemical nature of the contents. In no single case where sulfuric acid was the sole or main component was the fact disclosed on the label. In a few cases, samples containing this acid as an active constituent bore labels which misrepresented the nature of the contents. In Kedah a mixture of sulfuric and formic acids was on sale as "90" Formic Acid. In Perak, two mixtures, one of sulfuric and formic acids and the other of sulfuric and acetic acids were sold as "Acetic Acid 99%" and "90% Formic," respectively; in Selangor, a sample of sulfuric acid was sold under the label "Acetic Acid B." This indicates that those who bottle sulfuric acid for sale to small holders are by no means anxious to advertise the fact but rather to hide it.

Among the samples which were found to consist of formic and acetic acids, there were again a few cases of misdescription. In Pahang three samples of formic acid were described as "Acetic Acid," "Best Acetic Acid" and "Japanese Acid," respectively, and one sample of acetic acid was sold as "Cat Formic;" in Negri Sembilan one sample labeled "Acetic Acid" was found to consist of formic acid.

There is at present no legal obligation on the bottler of coagulants to describe on the label the nature and strength of the active principle, and those bottlers whose coagulants are sold under brand names only and who do not attempt to disclose the chemical nature of the materials used, commit no breach of the law; those on the other hand who sell say sulfuric acid in the guise of acetic acid, could probably be punished by law for such misdescription. They are, however, in a minority.

#### **Individual Coagulants and the Extent of Their Use**

In order to obtain an indication of the extent to which the various coagulants are in use, the acreages of rubber on estates of less than 100 acres, as shown by the Rubber Statistics Handbook 1935, and the coagulants favored are shown by States in the following table.

Acreage of Rubber on Estates of Less than 100 Acres							
Coagulants Favored	Kedah	Perak	Selangor	Negri Sembilan	Pahang	Malacca	Johore
Acetic and formic acids	...	...	157,850	82,707	76,902	74,985	...
Mainly sulfuric acid	100,691	254,886	...	...	...	...	...
Mainly acetic and formic acids but sulfuric acid also used in appreciable amounts	...	...	...	...	...	...	392,589
							392,589

It would seem that on roughly one-third of the total acreage of small holdings, the coagulants are those employed by European-owned estates. In the four territories, Selangor, Negri Sembilan, Pahang, and Malacca, which make up this acreage, the position with regard to coagulants is very satisfactory.

In one-third of the total acreage, the favored coagulant is sulfuric acid. This acid is sold in a number of forms. It is found in the main as a simple mixture of sulfuric acid and water. It also occurs under different names in admixture with small amounts of hydrochloric acid. The composition of these brands is 53-54 per cent sulfuric acid, together with amounts of hydrochloric acid up to 1.5 per cent. Curiously enough one of these mixtures is named "Coagulatex" and in 1918 Eaton, Grantham, and Day (Dept. of Agriculture, Federated Malay States, Bull. no. 27, April, 1918) described tests on a proprietary coagulant which bore this name and had an almost identical composition. It is probable that this preparation may have survived since that time. Sulfuric acid also appears in preparations which contain in addition, acetic, or formic acids. These mixtures, like those containing sulfuric and hydrochloric acids, are designed to simulate pure acetic and formic acids in pungency, appearance, and effectiveness, while allowing greater profit to the bottler. It is surprising that sulfuric acid is in such common use over such a large area, and the indications are that it has been in common use for some years. This is the outstanding feature of the survey. Though nobody has been aware of the fact, users have undoubtedly consumed thousands of tons of rubber prepared by the use of this acid during the last few years. There have been many signs of nervousness on the part of manufacturers when, during slump times, some large estates proposed to use this acid and a few actually did so. Tests carried out by manufacturers' organizations on specially prepared samples led to the issue of a strong request by the Institute that estates should refrain from the use of this acid; it was further requested that any estate which did employ it should declare the fact to the buyer at the time of consignment. The feeling among manufacturers is one of timidity towards this coagulant, even when it is known to be in the hands of comparatively skilled persons. That it should now transpire that it has been largely used for some time by the country's most unskilled producers is disturbing. It is tempting to infer that, because of the undoubtedly large amounts of sulfuric acid-rubber which have been consumed without serious outcry, the grounds for the prejudice against its use are not strong, but manufacturers may have had difficulties which have not been made known and which may perhaps be traceable to the coagulant. Further there can be no gainsaying the fact that the use of numerous coagulants of this type must militate against uniformity in Malayan rubber as a whole, and it would therefore be extremely unwise not to deter small holders from their use wherever possible. Fortunately, the Small-Holders' Advisory Service of the Institute, which has brought the facts to light, can be and is being employed actively to advise and persuade small holders in the territories concerned

to use formic and acetic acids only. There are already indications that the propaganda is having the desired effect.

Though in the remaining one-third of the total acreage of small holdings, the chief coagulants are formic and acetic acids, the popularity in some districts of Johore of certain brands which contain sulfuric acid, is rather disturbing.

In all districts, where organic acids are in use, formic acid is much more popular than acetic acid. Of seventy samples of acids found in the country, fifty-eight were of formic acid. On European estates formic acid has very largely displaced acetic acid and the same is apparently true of small holdings.

Alum enjoys only a minor popularity as a coagulant.

#### Summary

A survey was made of the coagulants employed by Malayan small holders. Though in the main these small holders are employing formic and acetic acids, sulfuric acid is employed to a much greater extent than has been supposed. Propaganda against the use of this coagulant was commenced recently through the Small-Holders' Advisory Service, and reports from the districts are encouraging.

# The Stability of Abiarana Gutta-Percha Latex

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## I

Although it has long been known that the rubber latices of different species of trees differ widely as to their stability, very little information can be found in the literature.<sup>1</sup>

We compared the properties, mainly the stability, of an *Abiarana gutta-percha* latex (*Lucuma lastiocarpa*, family *Sapotaceae*, fribe *Mimusops*) with those of the fairly well-known *Hevea brasiliensis* latex. (The *Hevea* latex we used was an ammonia-preserved latex of about 35 per cent dry rubber content.) As we had only a very small sample of about 40 cc. of the *Abiarana* latex, a second small sample of the same appearance and the same properties, the origin of which was not ascertained, was also used. We have good reasons to believe that it also was an *Abiarana gutta-percha* latex. For both samples and the analysis we are greatly indebted to W. H. Stevens,<sup>2</sup> London.

TABLE I  
ANALYSIS OF SAMPLE OF ABIARANA GUTTA-PERCHA LATEX

	Per Cent on the Latex
Total solids	37.1
Crepe (by acetone, washed on rolls and dried)	33.6
Whence total solids excess	3.5
Diffusate (70 hours) by direct measurements	3.4
Specific gravity	0.984
Acetone extract of dry crepe	2.2
Nitrogen content of dry crepe	0.20
Gutta hydrocarbon (by difference)	31.2

	Distribution of the Nitrogen:	
	Per Cent on Latex	Per Cent on Dry Material
Total solids	0.33	0.89
Crepe	0.20	0.59
Diffusate	0.17	4.97

According to W. H. Stevens' information, neither of the samples contained preservatives. Both had, when we got them, a  $p_H$  of about 5.3 and a strong smell of fermentation. They remained stable and unchanged in every respect during the many months we had them under observation. *Hevea* latex, on the other hand, coagulates within a few hours unless preservatives such as ammonia are added.

In the course of some days the *Abiarana* latex always creamed up, forming a very concentrated cream of about 80 per cent above an opaque, yellowish serum. On being shaken, the cream disperses again completely, and under the microscope only single particles in vivid Brownian movement are observed. They are perfect spheres of 1-2 $\mu$  diameter.

The behavior of the two latices towards electrolytes is even more markedly different. *Hevea* latex coagulates readily, forming one single lump of rubber above

a clear serum; if the latex is very dilute, the rubber forms coherent strings which curdle at once on slight agitation. *Abiarana* latex on the other hand cannot be coagulated irreversibly by electrolytes; if they are added, the *Abiarana* creams up rapidly; on shaking the cream readily redisperses; thereafter creaming-up, (which takes just as long as before) and redispersion can be repeated at will.

The cause of the different behavior of the two latices is recognized by microscopic observation; in a solution of  $p_H > 6$  both have almost exclusively single particles, and though occasionally two or more approach or even collide, they do not cohere, but either repel one another immediately or rapidly rotate together for some seconds and then suddenly separate again.

In a solution of a  $p_H$  of about 3.5 to 5, or in a solution of a  $p_H > 6$  with a suitable amount of salt, a difference becomes apparent. With *Hevea* latex a certain fraction of the collisions leads to irreversible aggregation, *i. e.*, the particles do not separate again; their joint Brownian movement is smaller and their creaming velocity higher. On creaming-up they collide with other particles or aggregates and thus grow larger and larger in course of time. If, however, very few particles are in the liquid (*e. g.*, in 1:5000 dilution), the number of collisions may be so small that a cream is formed containing not too large aggregates. These can be dispersed in the liquid by careful agitation, but, by shaking strongly, they unite to one single lump of rubber. Hence a sharp strong movement of the liquid can produce an even stronger effect than the Brownian movement, so that the total number of collisions depends on the concentration of the latex and on the movement of the liquid. The percentage of irreversible collisions depends on the degree of discharge of the particles caused by the addition of acid or salt. It increases with increasing discharge. Thus the velocity of coagulation depends on, at least, two factors: concentration of the latex and state of discharge. If the particles are so weakly discharged that coagulation is a slow process, it may be accelerated by shaking vigorously, because this greatly increases the total number of collisions, and hence the fraction of irreversible collisions too.

The *Abiarana* particles also, when acid or salt is added, form aggregates, depending on the concentration of the latex and the degree of discharge. The more concentrated and the more discharged, the more and the larger aggregates are formed, and, therefore, the higher is the creaming velocity. But these aggregates, or nearly all of them, are reversible, and either break up spontaneously or are dispersed by sharp agitation of the liquid, by collisions with other particles or aggregates, or by an impact with the wall. They, therefore, do not grow indefinitely in course of time, as is the case with *Hevea*; an equilibrium is established between association and dissociation. One fraction of collisions causes the breaking up of aggregates which have been produced by another fraction. The ratio of these two fractions determines the size and number of the aggregates. Such equilibrium conditions continue when the latex is shaken, and the redispersion of the aggregates seems to take place even more quickly than their formation, in contrast to the behavior of the *Hevea* latex.

The parallelism between state of discharge, aggregation and creaming velocity is very obvious (*cf.* Table II). A given  $p_H$  and latex concentration always involve a given distribution of the particles: a corresponding fraction of them unites to aggregates of characteristic sizes, the fraction of single particles also being characteristic.

The aggregates of *Abiarana* are much smaller than those of *Hevea*, even when the latter are observed immediately after being discharged, because in the *Abiarana* latex the number of collisions resulting in aggregation is much smaller. The particles dispersed by shaking show their old vivid Brownian movement and seem



TABLE II

PARALLELISM OF DEGREE OF DISCHARGE, AGGREGATION AND CREAMING VELOCITY OF AN ABIARANA LATEX (1:100 DILUTED)

Acetic Acid (in Millimol)	Creaming Velocity**	State of the Particles (Determined under the Microscope)
—	> 48 <sup>a</sup>	95 per cent of the units* are single particles. 5 per cent are present as aggregates. Most of them contain 2, and in a few cases 3, particles.
1.00	36 <sup>a</sup>	About 50-70 per cent of the units are single particles. Many aggregates contain 2 and 3 particles. Few bigger aggregates are present.
1.25	4 <sup>a</sup> 30'	About 30-50 per cent of the units are single particles. Many aggregates contain up to 12 particles, but most of them only 2-5.
1.43	3 <sup>a</sup> 20'	Only few units are present as single particles. Aggregates are formed up to 20 particles, and some even larger. Most of them, however, contain 3-9 particles.

\* Each aggregate, irrespective of its size, is counted as one unit, because otherwise the percentage of single particles would be very difficult to estimate.

\*\* The latex was discharged to a different degree by adding different amounts of acetic acid. Creaming velocity was determined as follows: the latex containing the acid was filled into normal test-tubes to a height of 2 cm., and the time was noted when the latex particles had creamed up so far that the lower 1 cm. of the liquid had become so transparent that print could be read through it. The time for complete creaming up was less characteristic because with decreasing concentration of particles the number of collisions also decreases, so that a certain percentage of unaggregated or poorly aggregated particles remains, the creaming velocity of which is small and ill-defined.

The second and third column of Table II do not seem to agree so strictly as expected. The comparatively high percentage of single particles observed under the microscope is partly due to the difference in experimental conditions. The number of collisions which can occur in the 1 mm. cavity of the slides, is much smaller than in a layer 2 cm. high. Once the particles have come close to the cover-glass, they are checked in their free movement and are rarely able to aggregate. The aggregates already formed, however, collide more frequently with the wall than they do in the test-tube, and therefore their chance of being broken up is bigger under the microscope than in the test-tube. For these two reasons, the number of single particles and the degree of aggregation on the whole must be different under the two conditions; more single particles and fewer and smaller aggregates will be seen under the microscope.

identical in every respect with the original single particles. We assume that the *Abiarana* particles do not approach each other so closely in the aggregates as do the *Hevea* particles, owing to strong hydrophilic layers around them though a magnification of 1100 shows no difference in the particle distance of *Hevea* and *Abiarana* aggregates; in both the particles retain their original shape.

We shall henceforth call the irreversible aggregation of *Hevea* latex "coagulation," and the reversible aggregation of *Abiarana* latex simply "aggregation."

TABLE III\*

AGGREGATION VALUES (MILLIMOLS PER LITER) OF AN ABIARANA LATEX (1:100 DILUTION)

KCl	BaCl <sub>2</sub>	AlCl <sub>3</sub>	Th(NO <sub>3</sub> ) <sub>4</sub>	CuCl <sub>2</sub>	Acetic Acid
100	15	0.66	0.11	2	1

\* These measurements were done in a simpler way than those in Table II. We determined the electrolyte concentration which caused the latex, diluted 100 times, to cream up within 2 hours. The test-tubes, containing latex + electrolyte in different concentrations, were stood in a row, and it was easy to fix the critical concentration which could cause a distinct change in the distribution of the particles, in the course of 2 hours, while that just below did not do so. In the experiments of Table III creaming-up had not proceeded so far as in those of Table II.



The particles of both *Abiarana* and *Hevea* are negatively charged and therefore the aggregation (creaming-up) also of the former mainly depends on the nature of the cations, specially their valency (cf. Table III).

A concentration of mono- and divalent cations larger than that given in Table III increases the creaming velocity. A considerably larger concentration of tri- and tetravalent cations and of  $H^+$ -ions diminishes the creaming velocity, because these cations are able to recharge the particles positively and thus to reduce or even to entirely prevent aggregation. The reversal of charge was proved by cataphoretic tests.

## II

What is the cause of the different stability of *Abiarana* and *Hevea* latex? The stability of *Hevea* seems to be mainly determined by proteins. With Scholz<sup>3</sup> we are inclined to assume that proteins sensitize the latex and render it rather hydrophobic. Scholz has found on comparing a protein-free *Hevea* latex with (a) an ordinary latex, and (b) with a protein solution, that the latex behaves as if it were sensitized towards all cations except the monovalent ones.

From the behavior of the *Abiarana* latex we conclude that it is most likely a protected hydrophilic system. A strongly adsorbed, hydrophilic layer round the particles prevents them from approaching each other so closely that the attracting forces becomes predominant. This simple assumption makes the behavior, described above, perfectly understandable. It also explains the fact that when migrating under the influence of an electric current, the particles of *Hevea* form a beautifully coherent skin on the anode (the phenomenon which renders the "anode process" feasible), while the particles of *Abiarana*, though they are also deposited on the anode to a certain extent, do not ever form a coherent skin, but remain separated from each other and readily redispersible.

The following experiment proves that (as in a normal protected suspension) the *Abiarana* particles have adsorbed a foreign substance, which is also contained in the serum. If the cream is separated from the serum and shaken up with water, the aggregates are easily redispersed and cream up again readily on adding acetic acid. If this washing process is repeated several times, the latex at last creams up rapidly without addition of acetic acid and is even partly coagulated. The *Abiarana* latex, then, when deprived of a protecting substance contained in the serum, behaves like *Hevea* latex, so that the difference in the stability of the two latices must mainly be due to the presence of a protecting substance in the *Abiarana* and not to other factors as, for instance, the different consistency of the particles.

This experiment proves further that the protecting substance is adsorbed reversibly, in a true adsorption equilibrium, a fact being by no means obvious. Consequently precise conclusions concerning the *Abiarana* latex in normal concentration cannot be drawn from the behavior of single latex particles in microscopic cataphoretic measurements. For these are carried out in a latex diluted 1000 times or more. This dilution corresponds to a strong washing out. Hence distinctly less of the protecting substance, which normally determines predominantly the properties of the latex, is left adsorbed on the particles. Kemp and Twiss<sup>4</sup> have drawn the same conclusions from the results of cataphoretic measurements with *Hevea* latex.

Another proof of the protecting action of the reversibly adsorbed substance is the fact that washed *Abiarana* latex coagulates readily on being boiled, whereas unwashed *Abiarana*, treated in the same way, remains stable.

That the protecting substance is actually contained in the serum can easily be

shown by the fact that if a sufficient amount of *Abiarana* serum is added to *Hevea* latex, the mixture is stable like the *Abiarana* latex itself; on adding acetic acid it does not coagulate, but only aggregates and creams up. A mixture of whole *Abiarana* latex plus *Hevea* latex behaves of course in the same way.<sup>2</sup>

A rough quantitative investigation shows that one part of *Abiarana* latex completely protects one part of *Hevea*, if both are in their original concentration (about 35 per cent). If diluted, less *Abiarana* is required *e. g.*, one part of *Abiarana* diluted 1:50 protects three parts of *Hevea* of the same concentration.

A mixture of *Hevea* latex with a sufficient amount of *Abiarana* latex or serum is, like pure *Abiarana*, stable on being boiled, unless it has been washed beforehand. On being washed, as described above, the mixture behaves similarly to *Abiarana* latex, the only difference being that less washing is necessary to remove so much protecting substance as to effect coagulation. After washing, the mixture coagulates in just the same way as does pure *Hevea*.

### III

We tried to find out the chemical nature of the protecting substance contained in *Abiarana* latex.

Since the charge of its particles can easily be reversed by  $H^+$ -ions, even after the latex has been dialyzed, one could assume an ampholytic substance of the protein type to be the responsible factor. It should, it is true, be a protein, which is much more hydrophilic than the protein which determines the behavior of *Hevea* latex.

The products of splitting proteins are usually more hydrophilic than the proteins themselves. Hence we investigated the reactions of *Abiarana* latex towards several specific reagents for proteins and the products of splitting them. In Table IV the behavior of *Abiarana*, *Hevea*, and peptone (BDH products) are compared.

TABLE IV

BEHAVIOR OF HEVEA, ABIARANA, AND PEPTONE TOWARDS REAGENTS FOR PROTEIN AND THE PRODUCTS OF SPLITTING PROTEIN

Reagent	Hevea	Abiarana	Peptone
Acetic acid	Coagulation	Microsc. aggregation	No precipitate
Formaldehyde	Coagulation	Microsc. aggregation	No precipitate
Thioalcylic acid	Coagulation	Stronger microsc. aggregation	No precipitate
Trichloroacetic acid	Coagulation	Small macrosc. aggregation	Slight precipitate
Phosphotungstic acid	.....*	Slight sediment	Slight precipitate
Biuret test	Violet-blue	Blue, coagulation	Violet-blue

\* Reaction only takes place in neutral or acid solution, in which *Hevea* is coagulated in any case.

The table reveals a marked resemblance of the reactions of *Abiarana* with those of peptone. Several other protein products also, not mentioned in the table, such as lysalbinic acid, etc., show similar reactions. We, therefore, tested whether *Hevea* later could be stabilized by protein products, as it is by *Abiarana* serum. No protecting action was observed with protalbinic acid, lysalbinic acid, peptone, or with any of the many amino acids tested in many different concentrations and after leaving them in contact with the *Hevea* particles for shorter and longer periods; in all cases *Hevea* coagulated readily on addition of acetic acid. None of these substances has a stabilizing action similar to that of the substance contained in *Abiarana*, and, therefore, none of them is probably of a similar chemical nature.

Though these experiments are incomplete, we consider it unlikely that any

protein disruption products are the cause, for a second reason: On dialyzing *Abiarana* serum through a collodion membrane the substance causing a positive biuret reaction<sup>6</sup> (see Table IV) passes through the membrane, whereas the unknown protecting molecules were unable to do so. We could not protect *Hevea* latex with the liquid outside the membrane, while it was possible to do so with the liquid inside, even after lengthy dialysis. The molecules of the protecting substance are therefore bigger than those of protein products; peptone and lysalbinic acid both pass through the membrane.

The protecting substance in *Abiarana* latex is probably also not a true protein, because the reactions of *Abiarana* for proteins are negative, and proteins do not so far as has been observed up to now, give a protecting action like that of the *Abiarana* serum. Nine grams of gelatin, for instance, per liter of 3 per cent *Hevea* latex does not prevent coagulation. The only difference compared with the coagulation of pure *Hevea* is that the system has to be strongly shaken, but this is only due to the high "viscosity," which stops Brownian movement and thus prevents the collision of the particles.

The same applies to other hydrophilic substances, *e. g.*, starch. The coagulation of a 3 per cent *Hevea* latex with 9 grams of starch per liter appears to be the same as without it.

Hence we must assume that the unknown protecting substance is of a nature distinctly different from that of the usual protecting agents.

#### IV

The results and conclusions of this investigation agree to some extent with those of Moyer who investigated many latices of the *Euphorbia* species. Applying the Mudd technic of the moving interface, he determined the wettability of the particles,<sup>6</sup> and concluded that the particles of some latices have hydrophilic, those of others more hydrophobic surfaces. Being interested in the latices chiefly from a botanical point of view, he has so far not correlated the observed surface phenomena with the stability of the latices. But Moyer's direct experimental evidence of the widely differing surface properties, though obtained for latices different from *Abiarana* enhances the probability of our assumption that the great stability of the *Abiarana* latex results from the very hydrophilic properties of its protecting agent.

Moyer also determined with 21 species of *Euphorbia* the cataphoretic mobilities as depending on the  $p_H$ , and thus the isoelectric point of their particles.<sup>7</sup> From a comparison of these curves he concludes that some latices behave as if these particles were completely coated by proteins, others as if protected by a mixture of several proteins or by a mixture of proteins with other ampholytes. A third group of latices is found to behave as if the particles were coated by non-proteins. In spite of the fact that we do not consider (for the reason mentioned above) the cataphoretic method to be quite correct for systems protected by reversibly adsorbed substances, we believe that Moyer's results hold qualitatively. Hence we can take it from him that other stable latices protected by non-protein substances exist.

#### Summary

1. The latex of *Abiarana gutta-percha* is more stable than that of *Hevea*. In the absence of preservatives *Abiarana* latex is stable for many months, while *Hevea* coagulates readily in a few hours. On addition of electrolytes, *Abiarana* only creams up and is readily and reversibly redispersed; *Hevea* is coagulated irreversibly. Under the influence of the electric current *Abiarana* does not form a coherent skin on the anode; *Hevea* does so easily.

2. The stability of *Abiarana* latex is due to a protecting substance reversibly adsorbed on the particles. This substance may be removed by allowing the particles to cream-up repeatedly and by separating the serum from the particles.

The serum of *Abiarana* (or the whole latex) added to *Hevea* latex strongly protects the latter and causes it to behave like *Abiarana* latex.

3. A similar protecting action in small concentrations cannot be produced by substances such as gelatin, peptones, lysalbinic acid, starch, etc. The chemical nature of the protecting substance could not be identified. It must have a large molecular weight, since it does not diffuse through membranes.

4. The reversible creaming-up of *Abiarana* latex is influenced by the cations of the electrolytes added according to their valency, in agreement with the fact that the particles are negatively charged.  $H^+$ -ion and ter- and tetravalent cations are able to reverse the electrical charge of the particles.

5. The difference in creaming velocity due to different electrolyte concentrations (*i. e.*, to different degree of discharge) seems to depend on the average size and number of aggregates of particles which are formed.

### References

- <sup>1</sup> Cf. for instance, E. A. Hauser, "Latex," Dresden and Leipzig, 1927.
- <sup>2</sup> W. H. Stevens, *India-Rubber J.*, **90**, 36 (1935).
- <sup>3</sup> Scholz, *Kautschuk*, **4**, 5 (1928).
- <sup>4</sup> Kemp and Twiss, *Trans. Faraday Soc.*, **32**, 890 (1936).
- <sup>5</sup> Since our *Abiarana* latex was several months old when we got it, we are unable to decide whether the protein degradation products were present initially or were decomposed from proteins by later fermentation.
- <sup>6</sup> Moyer, *Am. J. Botany*, **22**, 609 (1935).
- <sup>7</sup> Moyer, *ibid.*, **21**, 293 (1934).

# A Study of Deproteinized Rubber

Tadao Okita

SUMITOMO ELECTRIC WIRE AND CABLE WORKS, LTD.

## I. INVESTIGATION OF METHODS OF MEASURING WATER ABSORPTION

While studying various properties of deproteinized rubber, to be used in making rubber insulated wire with low water absorption, we found some points worthy of note in methods of measuring the water absorption of rubber and some distinctive properties of deproteinized rubber, particularly in connection with the mechanism of aging.

As shown by Lowry and Kohman (*J. Phys. Chem.*, **31**, 23 (1927)) and many others, water absorption by rubber is attributable mainly to water-soluble substances and protein in crude rubber. Consequently, rubber having reduced water absorption can be obtained by removal of these substances from crude rubber, and by addition of only materials having no capacity for water absorption, *e. g.*, silica powder and zinc oxide. We prepared washed deproteinized rubber and compared its water absorption with that of washed smoked sheet. However, we investigated first of all methods for measuring water absorption.

Methods for measuring the water absorption of rubber may be divided into two kinds. One is to measure the degree of water absorption from the weight increase of a test-piece of certain size after immersion in water; the other from the weight increase of a powdered test-piece, which absorbs moisture under a certain vapor pressure. We carried out our experiments, chiefly, according to the second method, which is quicker and more convenient for comparing the water absorption of rubber, and avoids the weight increase due to oxidation. In later experiments, however, we also used the dipping method.

### Experimental

We obtained deproteinized rubber from ammonia-preserved latex by heating with alkali solution to decompose the protein, coagulating it with acetic acid, and washing it perfectly with a universal rubber washer of stainless steel. Its nitrogen content was under 0.04%. For comparison we washed another test-piece of F.A.Q. smoked sheet on a rubber washing roll (nitrogen content about 0.4%).

Rubber-sulfur (92.5-7.5) mixtures were vulcanized at 148° C. in a press and their tensile properties determined (Fig. 1). Deproteinized rubber vulcanized more slowly, was softer, had lower tensile strength and a higher elongation than smoked sheet.

(a) *Drying Velocity.*—A vulcanized sample (No. 100, washed smoked sheet) was shredded on a calender in crepe form and 2 grams placed in a weighing bottle. This was put in a desiccator with concentrated sulfuric acid and evacuated at room temperature (1.0-3.0 mm.). The sample was taken out each 24 hours and its weight determined. (Table I.) Probably due to incomplete evacuation, there was some oxidation. Accordingly accurate measurements were impracticable, but it seemed that drying was perfect in two days. Deproteinized rubber, which shows less water absorption than washed smoked sheet, dries more rapidly.

(b) *Weight Increase by Oxidation.*—Vulcanizates from No. 100 (washed smoked sheet) and No. 200 (deproteinized rubber) were creped and subjected for 3 days to vacuum drying in a desiccator containing concentrated sulfuric acid, and their

weight increases in the desiccator at room temperature (Table II) were determined at atmospheric pressure.

TABLE I. DRYING VELOCITY OF WASHED SMOKE SHEET

Cure (in Hours)	Days of Drying			
	1	2	3	4
1	4.3	3.3	3.5	3.2
2	4.8	3.8	4.0	3.4
3	4.3	3.2	3.5	2.4
4	4.2	3.0	3.1	2.2
5	3.5	2.7	2.6	1.5

The data represent the decreases in weight in mg. of one-gram samples.

TABLE II.

WEIGHT INCREASES OF CURED RUBBER BY OXIDATION

Cure (in Hours)	Days of Drying					
	1	2	3	4	6	8
(A) No. 100 (Washed smoked sheet)						
1	0.2	0.3	0.2	0.2	...	...
2	0.3	0.7	1.2	0.8	...	...
4	-0.1	0.1	0.0	0.4	...	...
6	0.0	0.4	0.7	1.4	...	...
9	0.4	0.7	1.0	2.5	...	...
(B) No. 200 (Deproteinized rubber)						
1	...	0.2	0.1	0.4	1.4	4.2
2	...	0.3	0.3	0.8	3.8	8.6
4	...	0.5	0.8	1.8	7.4	17.6
6	...	0.7	1.5	3.6	11.9	26.9

The data represent the increases in weight in mg. of one-gram samples.

Both deproteinized rubber and smoked sheet oxidized even at atmospheric pressure at room temperature and therefore increased in weight. This phenomenon is particularly marked in case of deproteinized rubber. When the water absorption

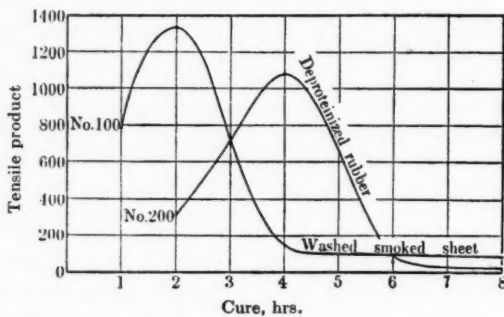


Figure 1

of rubber is measured by its weight increase account should be taken of this oxidation effect.

(c) *Velocity of Water Absorption.*—The foregoing experiments showed that oxidation is considerable in the water vapor method. Accordingly it is necessary to evacuate the air. There has been no report on the water-absorbing velocity in a vacuum, so an experiment was carried out in the following way.





Deproteinized rubber increases in water absorption capacity as vulcanization continues, and its weight increase owing to oxidation is also great during the measurements. The results are in accord with those obtained by Kohman on untreated rubber, in that overvulcanized rubber oxidizes rapidly and thereby increases in water absorption capacity.

The water absorption of rubber is reduced by deproteinization to about 0.05. This difference is decreased by vulcanization because deproteinized rubber is oxidized rapidly in the course of treatment, which counterbalances the decrease of water absorption resulting from hardening through vulcanization.

#### Relation between Aging and Water Absorption

A mixture of deproteinized rubber or washed smoked sheet 100, sulfur 3, zinc oxide 10, stearic acid 2, and benzothiazyl disulfide 1, was vulcanized at 139° C. and the optimum cure chosen. Ring-form samples 4 mm. thick at this optimum cure and also at a 10 minutes' overcure were aged by the Bierer-Davis method and the Geer method. After measuring the tensile strengths, they were washed, dried and their absorption over a saturated  $K_2SO_4$  solution measured by the same method as described (Tables II and III).

TABLE II  
RELATION BETWEEN AGING BY THE BIERER-DAVIS METHOD AND WATER ABSORPTION

No.	Aging (Hrs.) Cure (Min.)	Percentage			
		0	24	48	96
101	20	1.91	1.90	1.93	1.98
101	30	1.75	1.78	1.66	1.71
201	30	0.31	0.33	0.42	0.42
201	40	0.20	0.31	0.33	0.32

#### Water Absorption of Crude Rubber and a Rubber-Sulfur Mixture

By the method described we compared the water absorptions of crude rubber and a rubber-sulfur mixture over a saturated solution of  $NaCl$  or  $K_2SO_4$  at 30° C. or 35° C. The samples were all the same as were used for the first report (Table I).

TABLE III  
RELATION BETWEEN AGING BY THE GEER METHOD AND WATER ABSORPTION

No.	Aging (Hrs.) Cure (Min.)	Percentage			
		100	200	350	500
101	20	1.78	1.80	1.81	1.82
101	30	1.87	1.90	1.88	1.92
201	30	0.17	0.17	0.33	0.35
201	40	0.21	0.21	0.29	0.29

The water absorption was increased by aging, but these increases were comparatively small, whereas the weight increases due to oxidation were greater. Accordingly, the measurements obtained by Kohman and others in water under atmospheric pressure represent the sums of the weight increases by water absorption and oxidation. We cannot believe that they show true differences in water absorption.

It has been reported that vulcanized rubber is oxidized and forms sulfuric acid (cf. Yamazaki, *J. Soc. Chem. Ind., Japan*, 32, 1148 (1929)), and we assume that the increase of water absorption by aging is for the most part due to sulfuric acid thus produced.

In case of the base mixture containing accelerator, the water absorption of deproteinized rubber compared with washed smoked sheet was very small, in fact less than one-sixth as much, and even after aging it was less than one-fifth as much.

### III. MEASUREMENT OF WATER ABSORPTION BY THE IMMERSION METHOD

In the previous report, we compared the water absorption of deproteinized rubber and washed smoked sheet by the vapor method. In the present report, we measured the water absorption of industrial compounded rubber by the dipping method and ascertained experimentally the weight increases due to oxidation.

#### Experimental

Sulfur and other compounds were added to deproteinized rubber, washed smoked sheet, and specially treated rubber (washed to decrease its water absorption), as in the previous report the optimum cure was determined as before (Table I), sheets 1.5–2.0 mm. thick were vulcanized, and two discs 120 mm. in diameter of each were immersed in (1) distilled water at room temperature (5–35° C.), (2) 3.5% NaCl at room temperature, and (3) distilled water at 50 ± 0.5° C. Samples were removed from time to time, their surfaces dried, and the increases in weight determined. The percentage weight increases based on the original weight in the dry state were determined, and with the sum of the water contents in the original samples represented the total amount of water absorption.

The total weight increase by water absorption includes an increase in weight due to oxidation. Since the samples which were measured at room temperature showed blooming of sulfur and paraffin, accurate measurements could not be made, but there was no blooming at all at 50° C.

After such measurements the samples were vacuum-dried in a desiccator containing concentrated sulfuric acid at room temperature for a few days, and the differences in weight before and after vacuum drying were considered to be the true water content (Figs. 1, 2, and 3).

#### Discussion

According to Shôzô Satake (The Furukawa Electric Company, "Densen," Vol. III, 8 (1935)), the absorption velocity of vulcanized rubber sheet in its early stages may be represented by the following formula:

$$Q = k.s.t^n$$

where  $Q$  denotes the degree of water-absorption after  $t$  hours,  $s$  the area of the rubber,  $k$  a constant depending on the water-soluble components, and  $n$  a constant 0.50. Though Satake does not refer to the change in the constant  $n$ , it varies with the temperature. The relation between  $\log Q$  and  $\log t$  from the values measured at 50° C. is illustrated in Fig. 4. The foregoing equation is valid except for the value measured after a lapse of one day.

On the other hand, the value of  $n$  is smaller than 0.50, is not a constant in all cases, and differs greatly according to the crude rubber and compounding ingredients and also considerably with the presence or the absence of antioxidant. Accordingly, the rate of increase in weight of rubber sheet can be represented by the foregoing equation. For 2–12 days, however,  $n$  is a constant which depends on the temperature, crude rubber, and compounding ingredients.

Moreover, at 50° C. greater oxidation takes place than at room temperature, so the foregoing equation cannot be said to denote the true water absorption velocity but a resultant of the velocity of water absorption and oxidation. This is obvious from the fact that  $n$  changes with the presence or absence of antioxidant, in other words,  $n$  is also a function of the rate of oxidation.

The water absorption of deproteinized rubber is in every case below one-third that of washed smoked sheet, and that of the specially treated rubber was also small. But in neither case was there such a difference as was found for crude rubber

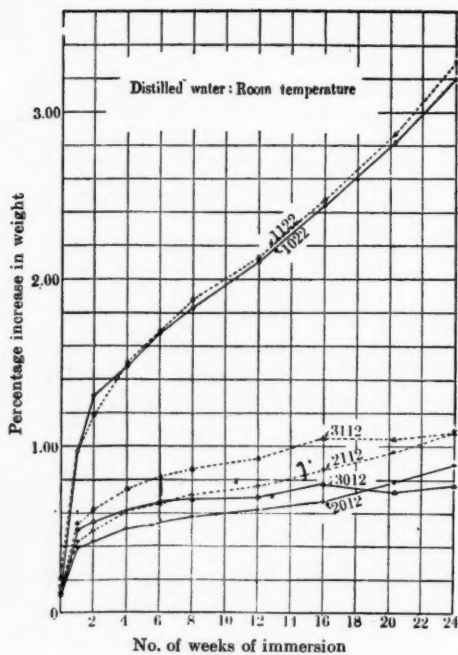


Figure 1

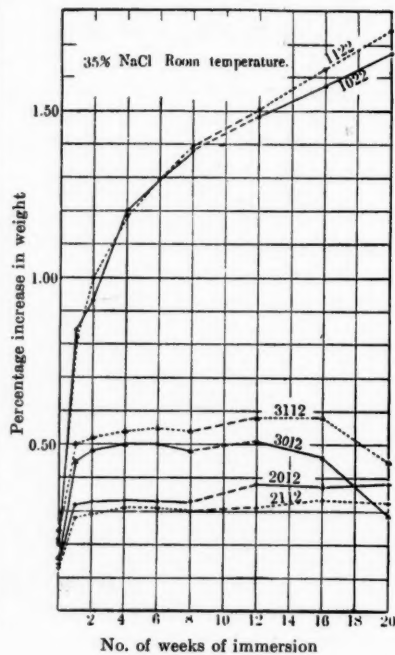


Figure 2

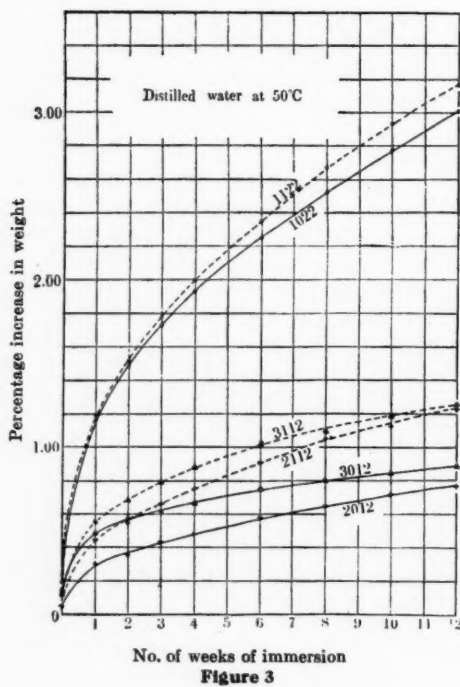


Figure 3

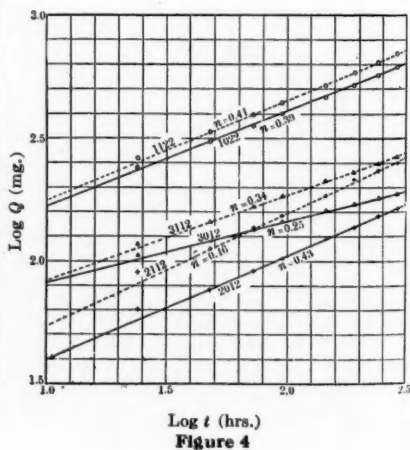


Figure 4

or the base mixture. This may be explained by the substances with water absorption properties present in compounding ingredients.

TABLE I

	1122	2112	3112	1022	2012	3012
Washed smoked sheet	100.0	...	...	100.0	...	...
Deproteinized rubber	...	100.0	...	...	100.0	...
Special treated rubber	...	...	100.0	...	...	100.0
Sulfur	3.0	3.0	3.0	3.0	3.0	3.0
Zinc oxide	25.0	25.0	25.0	25.0	25.0	25.0
Softener, etc.	11.0	11.0	11.0	11.0	11.0	11.0
Antioxidant	...	...	...	1.0	1.0	1.0
Accelerator	1.0	1.0	1.0	1.0	1.0	1.0
Total	140.0	140.0	140.0	141.0	141.0	141.0

#### IV. COMPARISON OF AGING

In Parts I and II, it was found that deproteinized rubber is more oxidizable than washed smoked sheet. But according to further experiments and the publication of Yamazaki, the aging of vulcanized rubber does not always conform to the oxidizability of crude rubber. In the present report, the aging properties of the vulcanized rubbers were compared.

#### Experimental

(A) *Comparison of Aging of Simple Mixes Containing Accelerators.*—Mixes containing deproteinized rubber or washed smoked sheet, 100; sulfur, 3; zinc oxide, 10; stearic acid, 2; benzothiazyl disulfide, 1, were vulcanized at 139° C. to 4 mm. sheets. Schopper rings from these sheets were tested for tensile strength. (Fig. 1).

In this case the vulcanization is retarded when the rubber is deproteinized, as in the case of rubber-sulfur mixes. This vulcanized rubber is softer, has a lower strength, and is more extensible than smoked sheet.

Optimum-cured and slightly over-cured (about 10 minutes) samples were aged by the Bierer-Davis method and Geer method (Figs. 2 and 3). By the latter method the deproteinized rubber deteriorated less than smoked sheet, but by the former method we could not recognize this difference. In view of these results it is not proper to compare the aging of vulcanized rubber by the oxidizability of crude or vulcanized rubber.

(B) *Comparison of Aging of Industrial Mixes.*—The mixes which were tested for water absorption in Report 3, were aged by the two methods (Figs. 4 and 5).

The industrial mixes, also gave the same results. By the Geer method deproteinized rubber deteriorated less than washed smoked sheet. By the Bierer-Davis method, when the rubber contained no antioxidant there was no difference between the two, but with an antioxidant, the deproteinized rubber showed slightly better aging properties.

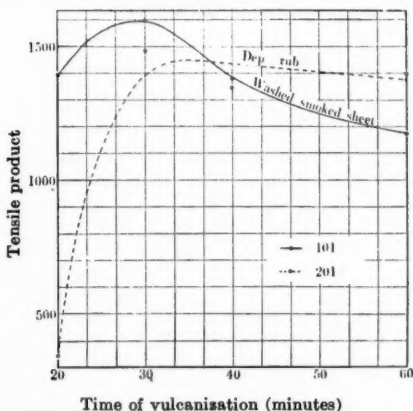


Figure 1—Curing Tests of Base Mixtures

### Conclusions

In Part I we assumed that deproteinized rubber would deteriorate more rapidly than washed smoked sheet. But the present experiments indicate that our supposition was not correct, because the former was more resistant than the latter to mechanical deterioration. The same result was true of the specially treated rubber.

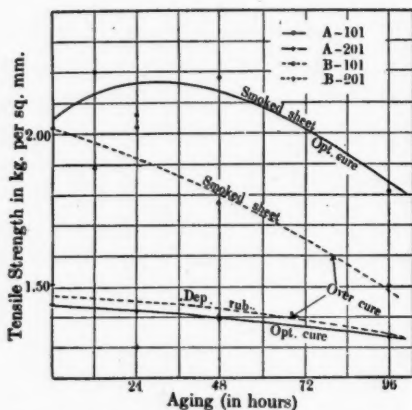


Figure 2—Aging of Base Mixtures by the Blerer-Davis Method

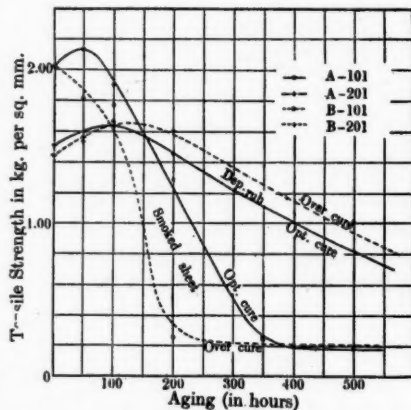


Figure 3—Aging of Base Mixtures by the Geer Method

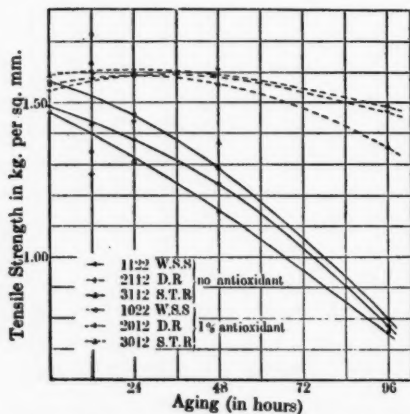


Figure 4—Aging of Industrial Mixtures by the Blerer-Davis Method

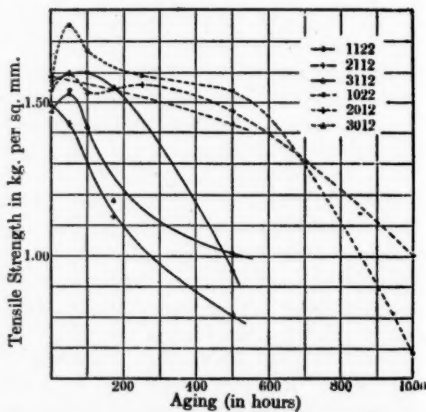


Figure 5—Aging of Industrial Mixtures by the Geer Method

It can be assumed that this depends on differences in the aging of the rubber hydrocarbon itself. But for several reasons, it is more likely that the major causes are differences in impurities and uniformity of cure. From several reports concerning protein in crude rubber by Stevens and others (Stevens, *Kolloid Z.*, **14**, 91 (1914); Park and Sebrell, *India-Rubber J.*, **73**, 265 (1927); Pickles, *Trans. Inst.*



*Rubber Ind.*, **3**, 60 (1927)), water-soluble protein would have an immense effect on deterioration.

Depolymerization and disaggregation would be the cause of deterioration by the aging of vulcanized rubber. This depolymerization, especially in artificial aging, cannot be explained merely by oxidation of the unsaturated part of the molecules, but must be attributed also to oxidation of combined sulfur, the formation of hydrogen sulfide, oxidation or other change in the free sulfur, metallic salts, proteins, and abietic acid.

It has already been shown that oxidizability increases with increase in the time of cure, and that there is no relation between oxidizability and optimum cure. It has also been found that addition of acid to rubber decreases the heat deterioration (unreported experiments). Moreover, it has been found that resistivity to deterioration is increased by smoking and that the most easily oxidizable mixes contain in the neighborhood of 7 per cent of combined sulfur (cf. Kohman, *J. Phys. Chem.*, **31**, 23 (1927)), lower percentages of combined sulfur resulting in greater resistance to deterioration (cf. Boggs, *Ind. Eng. Chem.*, **22**, 748 (1930)).

## Deproteinized Rubber

C. R. Boggs and J. T. Blake

SIMPLEX WIRE AND CABLE COMPANY, BOSTON, MASS.

**F**OR some years deproteinized rubber has been used by this company in the manufacture of rubber insulation, and the rate of consumption is increasing rapidly. This new and unique raw material is now also being manufactured for the Simplex Wire and Cable Company by The Goodyear Tire and Rubber Company on plantations in the Far East.

The special virtue of deproteinized rubber is its low water absorption and the electrical stability which it imparts to vulcanized rubber compounds immersed in water. Electrical engineers are specifying such compounds for submarine, underground, and duct cables and all other insulation that may be exposed to water.

The electrical properties of ordinary rubber insulation are impaired by increasing water absorption; the dielectric strength decreases, and the capacitance and leakance (or dielectric loss) increase. Power cables become useless when decreasing dielectric strength is insufficient to withstand operating voltage. Communication cables deteriorate rapidly by water absorption because their increasing capacitance and leakance prevent the practical transmission of signals long before dielectric strength is low enough to cause failure at the extremely low operating voltage of such cables.

### Historical

The development of the use of deproteinized rubber for this purpose has required a number of years. It had always been assumed that rubber was waterproof, and it was not until about 1918 that cable failures (both submarine and subterranean) were definitely connected with the absorption of water.

The writers' first attempts to reduce water absorption were by compounding with fillers, waxes, etc., but no real success was attained. The conclusion was eventually reached that absorption is due primarily to rubber itself. In 1924 the writers (2) discovered that absorption is caused principally by the proteins naturally present. Since it is hydrophilic in nature and is distributed in the rubber as a sort of network, the protein not only absorbs water but provides paths for its transfer throughout the mass.

The other nonhydrocarbon components of rubber, such as sugars and inorganic salts, have some effect by developing an osmotic action which naturally tends to cause absorption. Claiming that this osmotic action is the basic cause of water

absorption, Williams and Kemp (14) patented the excessive washing of rubber (13). After the publication of the writers' data (2), Williams and Kemp realized that osmotic action is not the principal cause, and they then considered the function of protein (5).

Since this basic discovery, many methods have been proposed and patented for the practical deproteinization of rubber. Any method is satisfactory, provided the rubber is unharmed by oxidation or heating, and that water-soluble or other hygroscopic substances do not remain in it as a result of the process.

### Composition of Raw Rubber

Raw rubber of commerce is not a pure substance. Besides the different molecular varieties of the hydrocarbon (rubber), there are present inorganic salts (ash), acetone-soluble fatty acids and resinous substances, organic water-soluble substances including sugars, and proteins or albuminoids. The proportions of these substances vary greatly and are larger for whole than for precipitated rubbers.

The amount of water-soluble substances may be from 0.2 to about 2 per cent. The ash ranges from 0.2 to about 1.5 per cent. The acetone-soluble portion is usually between 2 and 4 per cent.

The nitrogen content is seldom below 0.35 and may be 0.6 to 1 per cent. Based on the conventional factor of 6.25, this corresponds to a protein range of 2.2 to 6.2 per cent. Protein is not soluble in either acetone or water, but some of the nitrogen-containing substances are. The true protein nitrogen content of rubber should be determined on acetone-extracted rubber.

### Washing Rubber

For years it has been common practice for cable manufacturers to wash thoroughly the rubber used for electrical insulation. The Williams and Kemp patents (13) are, therefore, only an amplification of this custom. Since there are two types of substance in rubber responsible for its water absorption—viz., water-soluble substances removable by washing and proteins—the maximum effect of removing the former was investigated. Williams and Kemp (14) gave the following figures on the effect of washing smoked sheet:

Time of Washing Hours	Absorption from 3.5% Aqueous NaCl in 14 Days % by weight
0	2.9
1	2.4
2	1.9
3	1.2

Rubber does not absorb so much water from sodium chloride solutions as it does from pure water, and the solute tends to mask the effect of protein on water absorption.

Kemp states that the proteins in rubber "often cannot be removed by simple washing" thus implying that they usually can be so removed. The writers find that they cannot be.

In accordance with the instructions in the Williams and Kemp patents, large lots of smoked sheet, pale crepe, and sheeted Para biscuit were soaked in fresh water for 4 weeks. The soaking water was replaced with fresh water every week. The rubbers were then washed with hot (65° C.) water on a four-roll washer for 4 hours, and samples were removed every hour. (Ten-minute washing under these conditions is considered good commercial practice.) Nitrogen determinations were made on each of the samples and corrected by reagent blanks. Each value is the average of two determinations agreeing within 0.006 per cent.

The water-absorbing properties of these samples were also determined by a quick and practical test which has been used for years. A sheet about 2 mm. (0.080 inch) thick pressed between aluminum at 102° C. was soaked in distilled water for 20 hours, and the increase in weight determined. This increase was calculated on the basis of the area exposed to water, since for short periods area, and not total weight or volume, seems to be the controlling factor.

The values obtained are given in Table I.

TABLE I. WATER ABSORPTION OF SAMPLES

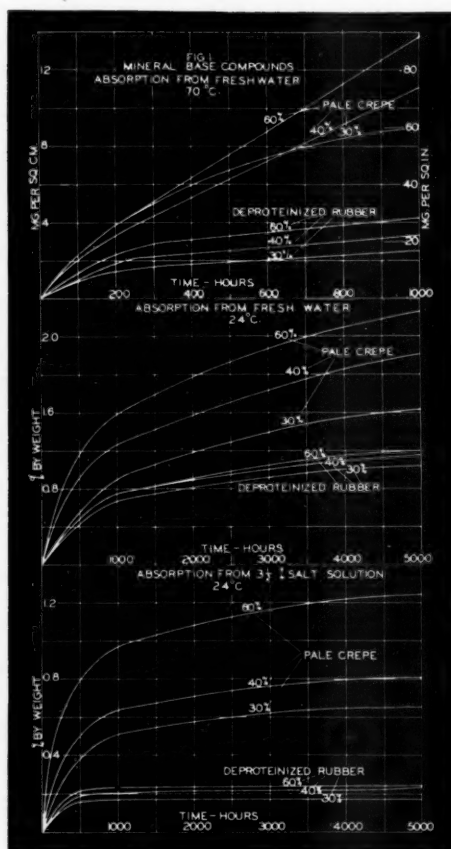
Rubber	Time of Washing Hours	Nitro- gen %	Gain in Weight	
			Mg./sq. in. of surface	Mg./sq. cm. of surface
Smoked sheet	0	0.387	25.0	3.87
	1	0.376	16.8	2.60
	2	0.373	17.8	2.76
	3	0.363	17.2	2.67
	4	0.357	14.7	2.28
Pale crepe	0	0.303	20.2	3.13
	1	0.285	17.4	2.70
	2	0.290	16.0	2.48
	3	0.290	17.2	2.67
	4	0.296	18.0	2.79
Para	0	0.333	29.1	4.50
	1	0.328	27.4	4.25
	2	0.324	21.7	3.36
	3	0.322	21.4	3.32
	4	0.318	20.6	3.19

There is a slight, but inappreciable, decrease of the nitrogen in each case due to the washing. Since there may be nitrogen-containing substances in rubber other than protein, it is possible to reduce the nitrogen content slightly without deproteinizing, but it is impossible to deproteinize without removing nitrogen. The water absorption does decrease to some extent, but the improvement occurs in the first one or

two hours of washing. It is clear that washing does not deproteinize rubber, nor does it reduce water absorption to as low a value as desirable.

### Deproteinizing Rubber

The deproteinization of rubber is not new. The classic method involves the use of solvents. Years ago Weber noticed that rubber is not completely soluble in organic liquids. Harries purified rubber by dissolving it in benzene and, after long standing, precipitated it from the clear supernatant liquid with alcohol or acetone. Midgley (8) improved this



method by finding that, for a rubber solution in a benzene-alcohol mixture, there is a critical temperature below which extensive precipitation of rubber hydrocarbon may occur. By controlling the temperature carefully, the rubber can be fractionally precipitated to give a substance containing 0.015 per cent nitrogen or less.

Protein may also be removed by chemical hydrolysis and elimination of the degradation products. Pummerer and Pahl (10) used sodium hydroxide at 50° C., dialyzed out the soluble substances, and obtained rubber containing 0.077 per cent nitrogen. Cummings and Sebrell (3) modified the process to give a substance containing less than 0.01 per cent nitrogen, much of which was acetone-soluble. Miedel, Geer, and Kemp (9) used alkaline solutions, and McPherson and Malm (6A, 7) used water or an aqueous salt solution. If the time and temperature of the hydrolysis are severe, the rubber tends to become soft and sticky, and therefore not satisfactory for commercial use.

Rhodes (11) tried unsuccessfully to deproteinize latex on a commercial scale by the use of proteolytic enzymes such as bromalin and papain.

The creaming of latex, either by centrifuging or by the use of pectins or alginates, brings about deproteinization. Although protein is not water-soluble, a portion of it seems to be dispersible in the serum, and its specific gravity is such that it passes into the dilute phase during the process and is discarded with the water-soluble components. The cream from either of these processes (of about 60 per cent rubber content) may be diluted, and the process repeated to obtain further purification. The creaming process has the disadvantage that the reagent is of a protein nature, which naturally hinders protein removal beyond a certain point. These two processes have the advantage of not degrading the rubber by heat.

McGavack (6) gave values for the nitrogen content of latex creamed with alginates. They are compared in the following table with results obtained by the writers on rubber from centrifugal latex:

Times Treated	Nitrogen Content	
	Creamed latex %	Centrifuged latex %
1	0.33	0.20
2	0.24	0.14
3	0.10	0.098
4	..	0.088
5	..	0.080

Deproteinized rubber may be recovered from purified latex by any of the common methods of precipitation.

### Drying Deproteinized Rubber

The drying of deproteinized rubber is a problem. Since such rubber absorbs water at a much slower rate than does the ordinary variety, it is correspondingly difficult to remove water from it. Vacuum-drying is regularly used. One obvious method of accelerating drying is to use sheets of minimum thickness. As a rough approximation it has been found that the difficulty of drying increases as the square of the sheet thickness.



### Properties

Deproteinized rubber is more nearly pure hydrocarbon than are the commercial varieties of plantation rubber; otherwise it has essentially the same chemical composition, as shown by the following percentage analyses of typical samples of deproteinized rubber and smoked sheet:

	Deproteinized Rubber	Smoked Sheet
Nitrogen	0.083	0.39
Protein (nitrogen $\times 6.25$ )	0.52	2.8
Ash	0.1	0.36
Water extract	0.12	0.64
Acetone extract	2.8	2.96

The reduction in the protein content is reflected directly in a reduction in the water absorption of raw rubber, as illustrated below according to the test used for Table I:

	Nitrogen %	Water Absorption—	
		Mg./sq. in. surface	Mg./sq. cm. surface
Smoked sheet	0.39	25.0	3.88
Deproteinized rubber	0.083	2.9	0.45

When these values are compared with those obtained simply by washing rubber (Table I), the beneficial effect of deproteinization is evident.

Before processing, a typical sample of deproteinized rubber had a plasticity of 3.4 by the Williams method, whereas sheet

TABLE II. PHYSICAL PROPERTIES OF INSULATING COMPOUNDS

Rubber in Compound	Type of Rubber	Optimum Cure at 270° F. (132.2° C.)	Tensile	Strength	Modulus (300%)	Elongation
%		Minutes	Lb./sq. in.	Kg./sq. cm.		%
Pure gum	Sheet	30	3160	222	240	760
	Deproteinized		3450	243	300	680
85	Crepe	80*	2860	201	220	740
	Deproteinized		2680	188	240	750
60	Crepe	40	3190	224	570	600
	Deproteinized		2970	209	380	690
40	Sheet	30	2360	166	680	560
	Deproteinized		2430	171	750	570
35	Sheet	30	2010	141	540	690
	Deproteinized		1820	128	520	710
30	Sheet	30	1820	128	700	540
	Deproteinized		1770	124	740	510
30	Sheet	45	1830	129	770	520
	Deproteinized		1700	120	730	510

\* At 275° F. (135° C.).

as received from the plantation gave a value of 6.6. This variation is reflected in a somewhat shorter breakdown, which is a definite commercial advantage.

Examination of samples of unvulcanized deproteinized rubber which have been in storage for over a year has shown them to be the same as when freshly prepared.

### Vulcanization

Deproteinized rubber vulcanizes normally with organic accelerators, although presumably most of the natural accelerators are removed in the preparation. Data on the tensile strengths, moduli, and elongations at break of typical insulating compounds of varying rubber content are given in Table II. The compounds were prepared both with regular commercial plantation rubbers and with deproteinized rubber. Tear, resistance, resilient energy, and hardness values for the pure gum compounds given in Table II are as follows:

Rubber	Tear		Resilient Energy	Shore Hardness
	With grain	Across grain		
Sheet	114	94	337	55
Deproteinized	110	105	445	58

### Aging

Deproteinized rubber compounds, containing conventional organic antioxidants in normal percentages, resist accelerated aging tests almost as well as those prepared from regular rubbers. Although the antioxidants naturally present in raw rubber may have been removed to some extent by the deproteinization, there is no apparent effect on the compounds.

TABLE III. AGING DATA

Rubber in Compound	Kind of Rubber	Aging Test	Values after Aging —					
			Original Tensile Strength	Tensile strength		Elongation		Decrease in tensile strength
				Lb./sq. in.	Kg./sq. cm.	Lb./sq. in.	Kg./sq. cm.	
%						%	%	
Pure gum	Sheet	4 days O.B.	3160	222	2850	200	630	10
	Deproteinized		3450	243	2430	171	610	29
85	Crepe	5 hours A.B.	2860	201	2730	192	670	5
	Deproteinized		2680	188	2440	172	700	9
	Crepe	5 days 250° F.	2860	201	2380	167	550	17
	Deproteinized		2680	188	2180	153	560	19
60	Crepe	2 days O.B.	3190	224	2710	191	580	15
	Deproteinized		2970	209	2540	179	660	15
40	Sheet	8 days O.B.	2360	166	1880	132	530	20
	Deproteinized		2430	171	1770	124	490	27
35	Sheet	21 days O.B.	2010	141	1620	114	450	19
	Deproteinized		1820	128	1630	115	460	11
	Sheet	5 hours A.B.	2010	141	1740	122	490	13
	Deproteinized		1820	128	1670	117	450	8
30	Sheet	8 days O.B.	1820	128	1450	102	460	20
	Deproteinized		1770	124	1480	104	440	16
	Sheet	3 hours A.B.	1820	128	1110	78	450	39
	Deproteinized		1770	124	1080	76	440	39
	Sheet	8 days O.B.	1830	129	1560	110	450	15
	Deproteinized		1700	120	1390	98	460	18
	Sheet	3 hours A.B.	1830	129	1040	73	400	43
	Deproteinized		1700	120	900	63	310	47

The aging data in Table III on the insulating compounds under a wide variety of conditions illustrate this point. The oxygen bomb (O.B.) was operated at 70° C. (158° F.) at a pressure of 300 pounds per square inch (21 kg. per sq. cm.), and the air bomb (A.B.) at 126.7° C. (260° F.) with 80 pounds

(5.6 kg.) pressure. The 121.1° C. (250° F.) aging was in a Freas oven with a circulating air current.

### Water Absorption

The difference between ordinary commercial rubbers and deproteinized rubber is most noticeable when they are exposed to water. If soaked in distilled water at 70° C. for 20 hours, commercial raw rubbers absorb 17 to 30 mg. per square inch (2.6 to 3.8 mg. per sq. cm.). Deproteinized rubber absorbs only about 3 to 5 mg. per square inch (0.46 to 0.75 mg. per sq. cm.).

The low water absorption of vulcanized compounds containing deproteinized rubber is their principal feature. Vulcanization decreases the rate of water absorption, and this decrease continues even through the overvulcanized state. A temperature increase accelerates the absorption. The rate of increase is logarithmic and doubles for about each 22–25° C. rise in temperature. Attempts have been made to relate mathematically the rate of absorption, time, and thickness of the sample. Probably no single equation can cover all cases, since there seem to be two classes of absorption. In one class the curve of absorption *vs.* time is of the die-away type and reaches an equilibrium value. The Andrews and Johnston equation derived from Fick's law of diffusion (1) fits these curves reasonably well. In many other cases, particularly in fresh water at elevated temperatures, absorption apparently proceeds indefinitely. It follows the relation:

$$x = bt^K$$

where  $x$  = amount absorbed

$t$  = time

$b, K$  = constants

A series of mineral base compounds containing whiting and zinc oxide as the principal fillers was prepared. Washed pale crepe and deproteinized rubber were used in different percentages to demonstrate the effect of variation in the rubber content.

Water absorptions in distilled water at 24° and 70° C. and in salt water at 24° C. on sheets 2 mm. thick are shown in Figure 1.

Similarly a submarine type of insulating compound was prepared with each of the two rubbers. Their water absorptions under the same conditions are illustrated in Figure 2. The benefit obtained by the use of deproteinized rubber in these compounds is clearly illustrated.

### Electrical Properties

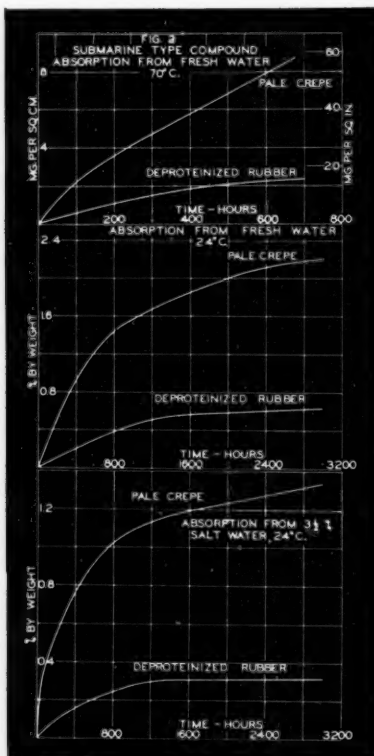
Unvulcanized deproteinized rubber is one of the best dielectrics known. Its dielectric constant is about 2.37 (close to the square of the index of refraction), its power factor about 0.15 per cent at 1000 cycles, its conductivity  $2 \times 10^{-17}$

mhos, and its dielectric strength about 1000 volts per mil. Vulcanization to soft rubber tends to increase slightly the dielectric constant and power factor in the same manner as with ordinary rubbers. Compounding with fillers affects the two types of rubber electrically in the same manner.

The difference between the electrical properties of deproteinized rubber and of ordinary commercial rubbers is definite but not large. Curtis and McPherson (4, 6A) report as follows:

Rubber	K	Power Factor %	Conductivity Mhos
Para	2.43	0.14	$3 \times 10^{-18}$
Crepe	2.43	0.16	$5 \times 10^{-18}$
Sheet	2.38-2.53	0.16-0.19	$0.3-1.0 \times 10^{-11}$
Deproteinized	2.37	0.15	$2 \times 10^{-17}$

The index of refraction seems to be controlled by the hydrocarbon, since it is changed very little when rubber is depro-



teinized. McPherson obtained an average value of 1.519 for commercial rubbers and 1.5184 for specially purified rubber.

The effect of 1000-hour immersion on the dielectric constant of the compounds whose water absorption is given in Figures

1 and 2 was determined. Sheets 1 mm. thick were used in water electrodes containing tap water at 24° C. The weight percentage of water absorbed after 1000 hours was also measured on duplicate sheets of this same thickness. The values are as follows:

Compound	Type of Rubber	Rubber Content %	Increase in K %	Water Absorbed % by weight
Mineral base	Crepe	30	16.0	0.92
		40	13.8	1.28
		60	7.6	1.6
	Deproteinized	30	-0.8	0.66
		40	-0.4	0.76
		60	+1.5	0.76
Submarine type	Crepe	..	5.2	1.66
	Deproteinized	..	1.4	0.45

The decreased water absorption of the compounds containing deproteinized rubber is reflected directly in the almost perfect stability of the dielectric constant. Mineral base fillers seem to be disadvantageous in the pale crepe compounds, since the dielectric constant increases least in the 60 per cent compound, although the water absorption is greatest. In the deproteinized rubber compounds the percentage of rubber is not significant.

### Oxidation

Compounds containing deproteinized rubber resist oxidation as well as do other compounds. As a matter of fact, submarine cables oxidize very little because temperatures are low and only a small amount of air is dissolved in the water. For example, gutta-percha, which is exceedingly sensitive to oxidation, lasts for many years on submarine cables. Evidence has been obtained showing that, if for any reason oxidation of rubber compounds does occur, the rate of water absorption has a slight tendency to increase.

### Applications

Besides the obvious and primary use of deproteinized rubber in electrical insulation exposed to water, there are other possibilities for its practical application. Stevens and Parry (12) investigated the characteristic odor of rubber goods and found that a definite part of this is due to the raw rubber itself. By removal of protein and by judicious use of compounding agents, entirely odorless articles may be secured. Undoubtedly, the public will soon demand odorless rubber toilet goods.

The physical properties of vulcanized rubber are seriously impaired by absorption of water; tensile strength, tear resistance, and abrasion resistance are decreased materially. For rubber compounds which must maintain these properties under more or less continuous exposure to water (particularly warm or hot water), deproteinized rubber is the only proper ingredient.

Many surgical rubber goods need to be sterilized repeatedly. Ordinarily, the life of such articles is limited. The use of deproteinized rubber will be effective in prolonging their service.

Ebonite is usually resistant to water absorption, but, when the water is warm, absorption may be a serious consideration. Deproteinized rubber overcomes this objection.

### Literature Cited

- (1) Andrews and Johnston, *J. Am. Chem. Soc.*, **46**, 640 (1924).
- (2) Boggs and Blake, *Ind. Eng. Chem.*, **18**, 224 (1926); Canadian Patent 277,204 (1928); U. S. Patent 1,997,355 (April 9, 1935).
- (3) Cummings and Sebrell, *Ind. Eng. Chem.*, **21**, 553 (1929).
- (4) Curtis and McPherson, Bur. Standards, *Tech. Paper* **299** (1925).
- (5) Kemp, *J. Franklin Inst.*, **211**, 37 (1931).
- (6) McGavack, *Ind. Eng. Chem.*, **27**, 894 (1935).
- (6A) McPherson, Cummings, Wing, and Scott, *Bur. Standards J. Research*, **8**, 751-8 (1932).
- (7) Malm, U. S. Patents 1,752,531 (April 1, 1930) and 1,847,123 (March 1, 1932).
- (8) Midgley, *J. Am. Chem. Soc.*, **53**, 2733 (1931).
- (9) Miedel, U. S. Patent 1,947,949 (Feb. 20, 1934); Geer, *Ibid.*, 1,968,883 (Aug. 7, 1934); Kemp, *Ibid.*, 2,040,314 (1936).
- (10) Pummerer and Pahl, *Ber.*, **60**, 2152 (1927).
- (11) Rhodes, *Ann. Repts. Rubber Research Inst. Malaya*, **1934**, 136.
- (12) Stevens and Parry, *India Rubber J.*, **88**, 513, 541, 546 (1934).
- (13) Williams and Kemp, Belgian Patent 311,864 (1923); Luxembourg Patent 13,156 (1923); British Patent 223,044 (1924); U. S. Patent 2,031,916 (1936).
- (14) Williams and Kemp, *J. Franklin Inst.*, **203**, 35 (1927).



# Transparency of Rubber Compounds Containing Magnesium Carbonate

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**H**IGH-GRADE plantation rubber is a fairly transparent substance. When carefully plasticized on clean mills and subsequently pressed, sheets with a high degree of light transmission are obtainable. However, because it is unvulcanized, the rubber is almost worthless for most purposes.

The production of vulcanized transparent rubber goods was, up to only a few years ago, confined to thin-walled pure gum compounds obtained either by the dipping process from solutions of rubber in organic solvents, or by subjecting so-called "cut sheets" to a "cold-curing" operation.

Since the introduction of modern vulcanizing accelerators, activators, etc., and the possibility of thus materially reducing the necessary amount of sulfur needed for perfect cures, several attempts have been made to obtain transparent rubber by "hot vulcanization," either in air or by press-molding.

For example, Jones (7) obtained a British patent for the production of transparent rubber by hot vulcanization, using in his cures less than 1 per cent of finely divided zinc oxide as activator (average size of particles, 0.15 micron) and about 2 per cent or less of sulfur. Colton (2) investigated cures containing rubber, sulfur, and accelerators, and found that zinc oxide in excess of 0.5 per cent produced a noticeable opacity.<sup>2</sup> Although transparent rubber can be produced by keeping the zinc oxide and sulfur content at a minimum and using only a finely divided grade of zinc oxide, such rubber when vulcanized cannot approach many of the valuable characteristics of normally compounded products, such as abrasion resistance, tear resistance, hardness, etc.

Recently it was found that, when certain grades of magnesium carbonate, notably Japanese brands, are used as fillers in rubber compounds, a light-transmitting product is obtainable. Investigations of such compounds have resulted in the production of a yellowish, transparent grade of rubber which may contain as much as 40 per cent or even more of Japanese magnesium carbonate. High tensile strength, good

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<sup>2</sup> The possibility of producing fairly thick, transparent, vulcanized, pure rubber compounds in the presence of higher amounts of zinc oxide by using specific activators, such as du Pont's Barak, finds its explanation in the extremely small quantity of sulfur needed and the fact that these activators generally react with the zinc oxide, forming soluble zinc soaps or the like (Hauser and Wolf, *Kautschuk*, 7, 186 (1931)).

aging properties, and excellent wear resistance are said also to be characteristic of such compounds, which are the basis for the transparent crepe soles found in most Japanese tennis shoes and similar footwear.

Tanaka (11) has carried out considerable research on the use of magnesium carbonate in rubber compounding and places the main reason for the opacity of rubber upon the respective refractive indices of rubber and filler. His results indicate that, when a transparent filler with a refractive index nearly the same as that of the cured rubber is used, the compound will exhibit transparent tendencies. Vulcanized rubber possesses an index of refraction of about 1.52, and Tanaka's magnesium carbonate an index of 1.50 to 1.53. Tanaka also notes that some grades of this filler are poorer than others and attributes this phenomenon to the presence of crystalline magnesium carbonate which, being anisotropic, will not give in powdered form a sharp, measurable index. He states, as a result of a microscopic examination which seems to support his theory, that amorphous forms of carbonate produce far greater transparency than crystalline forms.

The great interest which was created by the introduction of transparent Japanese crepe soles on the world markets and the failure by one of the authors to reproduce the transparency of the Japanese compounds by incorporating specially prepared amorphous magnesium carbonate or several standard European brands, called for a more detailed study of this type of rubber compound. This paper presents the results so far obtained.

### Experimental Procedure

The three following basic mixes were made up and cured for 10, 20, 30, 40, and 60 minutes at 25 pounds per square inch in the press:

Mix No.	I	I	III
Pale crepe	100	100	100
Sulfur	1.5	1.5	1.5
Hexamethylene tetramine	0.5	0.5	0.5
Mercaptobenzothiazole	0.5	0.5	0.5
Zinc oxide (regular)	1.0	...	...
Zinc oxide (Kadox red label)	...	...	1.0
Stearic acid	1.0	...	1.0
Zinc stearate	...	2.0	...

The proportion of rubber, sulfur, zinc oxide, stearic acid, and accelerator, as well as the special combination of the latter, corresponds to the test formulas generally used in Japan.<sup>3</sup> The zinc was introduced in the form of two types of oxide differing in particle size, and as the stearate to determine whether the degree of original dispersion has an important bearing on the transparency of the cured stock. Compound III was finally selected as the basis for all further compounds since it gives most satisfactory tensile strengths and most uniform transparency over a wide range of cures (3500 pounds per square inch at 30 and 40 minutes).

Eighteen different brands of commercially available magnesium carbonate, four of which were of Japanese origin, were mixed

<sup>3</sup> See, for example, the pamphlets on "Carp Brand" magnesium carbonates, issued by Kishi-Hashi Shoten, Ltd., Kobe, Japan.

with the basic compound in the following proportions: 5, 10, 25, 40, 60, and 100 per cent by weight on the rubber content. Cures were made at 30 and 40 minutes, which represent the optimum tensile strengths of the basic mix.

The slabs were cured between clean, polished steel plates to 0.06-0.07 inch thickness and were used for the determination of their tensile strength.

The average tensile strengths for the 30- and 40-minute cures for a characteristic domestic and Japanese carbonate are graphically demonstrated in Figure 1.

The domestic sample shows the characteristics of a reinforcing pigment (4) (the tensile strength passes through a maximum with increased loading); the Japanese brand does not alter the tensile properties of the basic mix up to loading of 35 per cent. The domestic sample shows better tensile strengths over the total range of loading than the Japanese.

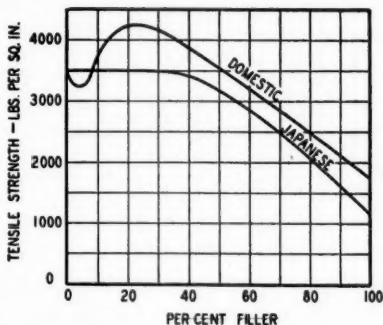


FIGURE 1. TENSILE STRENGTH OF FILLER COMPOUNDS

### Light Transmission

The slabs containing a loading of 25 per cent magnesium carbonate were also used to determine the total light transmission of all investigated varieties, for the purpose of selecting the most characteristic for detailed examination.

The transparency of the compounds was measured by means of the new Hardy recording spectrophotometer (5) which gives values for total light transmission over the visible range of the spectrum. The results are as follows:

Sample No.	% Trans- mission	Sample No.	% Trans- mission
Crude, milled, pressed crepe	49	9 <sup>a</sup>	36
Basic mix	40	10 <sup>a</sup>	12
1	39	11	34
2	42	12	24
3 <sup>a</sup>	45	13	34
4	48	14	26
5	36	15	35
6	20	16	8
7	35	17	27
8	28	18	13

<sup>a</sup> Mixes selected for further investigation.

Crude rubber (0.06 to 0.07 inch thick) passed 49 per cent of the light falling on it. Thirty-one per cent passed undeviated, 18 per cent was scattered. The same rubber, if compounded with 1.5 per cent sulfur and 1 per cent zinc oxide and accelerator, and vulcanized as mentioned, transmitted a total

of only 39 per cent, of which only 16 per cent was undeviated. It was first believed, that the zinc oxide present in fine subdivision was responsible for this phenomenon, but the fact that the same results are obtained when using soluble zinc stearate, for example, disproves such an assumption. The possibility remains that the cause for the reduction of total

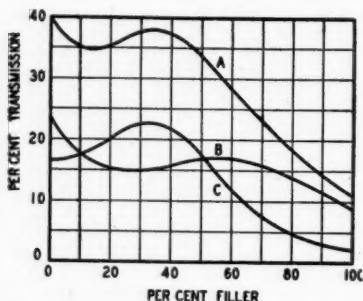


FIGURE 2. TRANSMISSION CURVES OF DOMESTIC MAGNESIUM CARBONATE AS FILLER

A—Total. B—Scattered. C—Undeviated.

transmitted light and the increase in scattering is due to the presence of sub-microscopic sulfur particles in the vulcanized compound (3). Samples 3 and 9 were selected for further detailed examination as representing the best Japanese and domestic samples, and sample 10 as representing the samples resulting in stocks of low transparency. With sample 9, curves for total and scattered light transmission with different per cent loading were obtained, from which the amount of undeviated light was calculated. The result is graphically shown in Figure 2.

Examination of these transmission curves reveals a decrease in total transmission with small additions of filler, then a rise, after which the transmission falls off smoothly. The amount of scattered light also falls off with small amounts of filler, but the undeviated light rises to reach a maximum of about 20 per cent between 25 and 40 per cent of added carbonate.

These observations might be explained in the following manner: With the first additions of filler the total transmission falls off because of light absorption by the magnesium carbonate. The scattered light decreases, owing to dilution of the rubber and consequently of the substance causing scattering within the sample. As more filler is added, the dilution effect becomes so pronounced that more light can penetrate the sample, thereby causing a rise in the total transmission. Since in this stage the effect of dilution is more pronounced than that of absorption, a rise in the transmission of undeviated light results. At high loadings, however, it becomes much more difficult to produce satisfactory dispersion of the filler during mixing; as a result, scattering increases because of agglomeration of particles. Because of the added effects of scattering and of absorption, total trans-

mission now falls off rapidly, and at 100 per cent filler a very low value is obtained, almost all the light being scattered.

Corresponding curves for compounds made with sample 3 (Japanese) show a striking difference (Figure 3). With small amounts of filler, both the total and scattered light transmission are sharply increased.

It might be possible that this type of carbonate removes the scattering agent from within the mix. This behavior, however, could not explain the increase in scattered light. If samples mixed with the Japanese carbonate are closely examined, it is evident that at low loadings (5 to 10 per cent) the surface is not as clear as those of the higher loadings. The increase in scattering is apparently caused, at least partially, by this surface effect. At higher loadings this

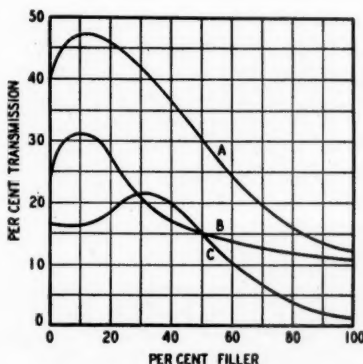


FIGURE 3. TRANSMISSION OF JAPANESE MAGNESIUM CARBONATE AS FILLER

A. Total. B. Scattered. C. Undeviated.

tarnish disappears, and the behavior over the remainder of the curves is similar to that observed in the domestic mixes (Figure 4). The identity of the substance causing surface scattering has not yet been established.

### Refractive Index

The refractive index of crude rubber, as used in these experiments, was determined with an Abbé refractometer. The rubber was pressed between the prisms to secure perfect optical contact. The refractive index ( $n_D^{25}$ ) was found to be 1.5115. Vulcanized rubber of the basic mix varied from 1.5236 to 1.5261, increasing with increasing time of cure. (The accuracy of measurements can be taken to be  $\pm 0.002$ .) Since working with compounds of higher loadings makes the readings more difficult, the results have only been evaluated to three decimal places:

30-Min. Cure			40-Min. Cure		
MgCO <sub>3</sub> Sample	Loading %	$n_D^{25}$	MgCO <sub>3</sub> Sample	Loading %	$n_D^{25}$
3	10	1.525	9	10	1.525
3	25	1.524	9	25	1.525
3	30	1.526			
9	10	1.525			
9	30	1.525			

According to the findings of McPherson and Cummings (9) and Kirchhof (8), the refractive index shows only small changes with the addition of different amounts of filler. (The

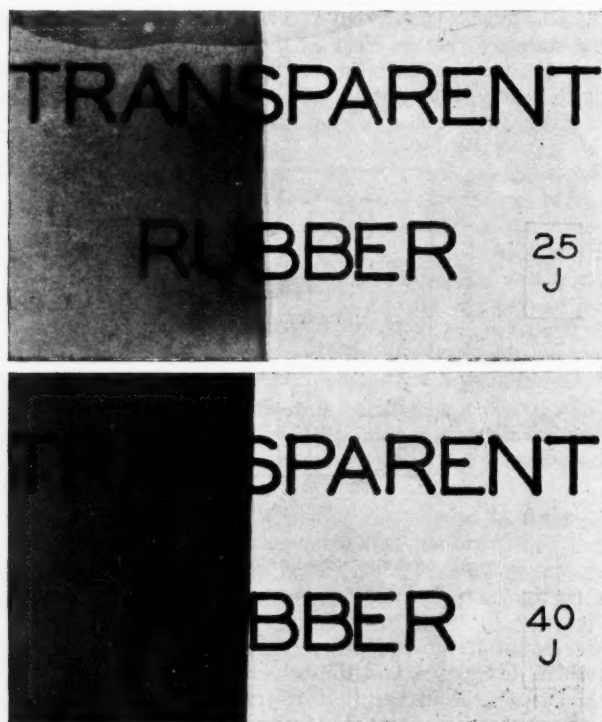


FIGURE 4. PHOTOGRAPHS TAKEN THROUGH TEST SLABS OF 0.06-INCH THICKNESS TO DEMONSTRATE THE TRANSPARENCY OF COMPOUNDS CONTAINING 25 AND 40 PER CENT OF JAPANESE MAGNESIUM CARBONATE, RESPECTIVELY

authors' crude rubber figure, 1.519, is somewhat lower than the one recorded by McPherson and Cummings and by Kirchhof, which presumably is caused by a difference in the crude rubber used.)

The refractive indices of the carbonates were determined by the immersion technic. Sample 3 (Japanese) gave an index between 1.515 and 1.530, which is in good accord with Tanaka's findings and with the results of Bratley and Thompson (1). Sample 9 (domestic) placed the index in the same



range. Sample 10 did not permit accurate determination. All the known basic and neutral magnesium carbonates are anisotropic and therefore possess more than one refractive index. Magnesite (6) has two—1.700 and 1.509. The trihydrate (biaxial) has the following indices (12): 1.526, 1.501, 1.412; the pentahydrate, 1.508, 1.470, 1.457. The indices for the basic carbonate  $2\text{MgO}\cdot\text{CO}_2\cdot 4\text{H}_2\text{O}$  (10) are 1.557, 1.534, 1.489; and for the compound  $4\text{MgO}\cdot 3\text{CO}_2\cdot 4\text{H}_2\text{O}$ , 1.566, 1.554, 1.538. With such materials it probably would be possible to place the index somewhere between the end values. No data have been located for the basic carbonate  $5\text{MgO}\cdot 4\text{CO}_2\cdot x\text{H}_2\text{O}$ . It is safe, however, to assume that the indices closely resemble those for the last compound mentioned.

### X-Ray Patterns

X-ray patterns (Debye-Scherrer) of the selected samples were taken and are shown in Figure 5. Pattern 1 corresponds to sample 3 (Japanese), and pattern 2 to sample 9 (domestic). The patterns are practically the same, and the corresponding structure was identified:  $5\text{MgO}\cdot 4\text{CO}_2\cdot x\text{H}_2\text{O}$  (10). Pattern 3, corresponding to sample 10 and resulting in stocks of low transparency, was identified as magnesite. However, careful examination reveals the presence of traces of the basic compound, as indicated by the arrows in the pattern of this sample.

The fact that the clearness of the lines in patterns 1 and 2 is decidedly inferior to those in pattern 3 reveals the fact that the particle size of the basic compound is much smaller than with the magnesite. The extreme fineness of the anisotropic crystals and the consequent difficulty of performing a satisfactory microscopic analysis seem to offer an explanation for Tanaka's erroneous assumption that carbonates giving stocks of high transparency are amorphous. The x-ray analysis also explains definitely why no satisfactory figures for the refractive index of sample 10 could be obtained by the immersion technic. With as widely differing indices as were established for magnesite, no other result could be expected by such a method.

Since these results are representative for a great number of actual tests, they seem to prove conclusively that good transparency in compounds, as used in this investigation, are obtainable only when basic magnesium carbonate of the general formula  $5\text{MgO}\cdot 4\text{CO}_2\cdot x\text{H}_2\text{O}$  is used.

### Water Content of Samples

The only remaining factor which might be responsible for the observed differences in light transmission and tensile properties of the Japanese and good domestic varieties is the actual water content of the samples. Since x-ray patterns do not permit accurate conclusions to be drawn in this respect, the method described by Menzel and Brückner (10) was

followed. Assuming a dry structure of  $5\text{MgO} \cdot 4\text{CO}_2 \cdot 3\text{H}_2\text{O}$ , sample 3 would correspond approximately to a formula of  $5\text{MgO} \cdot 4\text{CO}_2 \cdot 6\text{H}_2\text{O}$ , whereas sample 9 would carry 9 molecules of water.

This difference in water content might explain the higher light transmission of the Japanese brand and the initial increase in tensile strength with the domestic specimen of equal particle size.

If the Japanese carbonate is removing the scattering agent referred to, the mechanism of the process may be visualized

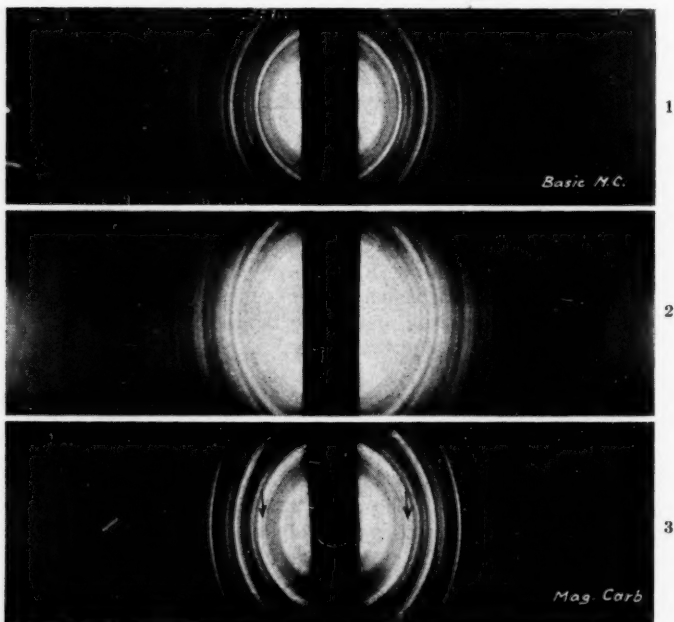
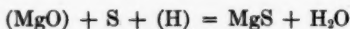


FIGURE 5. X-RAY PATTERNS OF SELECTED SAMPLES

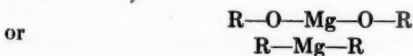
as a reaction between the filler and the substance causing scattering. If the latter is sulfur (which is probable), combination between it and the basic carbonate may occur under conditions of cure to form a substance soluble in the rubber:



Since the amount of water present in the domestic carbonate is greater than in the Japanese, more hindrance of the reaction would be found with the use of a domestic filler than with a Japanese. According to Menzel and Brückner (10) a basic carbonate such as  $5\text{MgO} \cdot 4\text{CO}_2 \cdot 6\text{H}_2\text{O}$  exists as a definite compound. This corresponds to the Japanese material. But the best domestic varieties contained water amounting to nearly nine molecules per unit of  $5\text{MgO} \cdot 4\text{CO}_2$ , the excess over six molecules probably being present as adsorbed water

in the filler. This excess water would impede the combination.

The initial increase in tensile strength in the domestic varieties might be due to the formation of additional bonds between rubber molecules; otherwise the diluting effect of the filler should weaken the mix. These bonds may be the result of oxygen-metal or plain metal linkages between the rubber molecules:



Such a combination would explain the rise of tensile strength, even with a small amount of reacting carbonate. Both of the suggested reactions would involve the combination of water. Since the domestic carbonate possesses excess water, mass action considerations suggest that this bonding would take place much more readily with this product.

### Other Phenomena

A few days after cure, several of the investigated samples, especially those showing the highest rise in tensile strengths, exhibited a crystalline bloom on the surface; this bloom was identified by microchemical analysis to be hexamethylene tetramine. Although more detailed work (now in progress) will have to be done to explain fully the mechanism of the reaction, it seems safe to assume that the activity of the basic group of the carbonate plays a predominant part.

Another interesting phenomenon is noticed with transparent magnesium carbonate mixes. When a piece of this rubber is stretched, it becomes white and opaque. If it is stretched only to moderate lengths and then the strain is released, it again becomes transparent. But if it is stretched severely, it no longer regains its transparency.

The fact that a severely stretched compound does not regain its transparency upon release of the strain unless heated, can be explained either by an irreversible change of the refractive index of highly stretched vulcanized rubber or by an orientation of the anisotropic filler particles in the direction of stretch, or both. Research towards a more detailed explanation of this phenomenon is now in progress and the results will be published later.

### Conclusions

1. Basic magnesium carbonates of the type  $5\text{MgO} \cdot 4\text{CO}_2 \cdot x\text{H}_2\text{O}$  will produce transparent vulcanized rubber.
2. Neutral carbonates of the magnesite type result in stocks of poor light transmission, even at low loading.
3. The basic carbonates, although of extremely fine particle size, are definitely crystalline in structure, as revealed by x-ray analysis.
4. The sample of magnesium carbonate producing the

best transparency was a Japanese variety. When 25 per cent by weight was compounded in rubber, an over-all transmission of 45 per cent was produced. None of the domestic varieties gave higher than 36 per cent, and only two samples out of the eighteen examined produced this value.

5. The best Japanese carbonate (sample 3) and the best domestic carbonate (sample 9) possessed the same structure—that of a basic magnesium carbonate of the general form  $5\text{MgO} \cdot 4\text{CO}_2 \cdot x\text{H}_2\text{O}$ .

6. The Japanese carbonate, corresponding to the formula  $5\text{MgO} \cdot 4\text{CO}_2 \cdot 6\text{H}_2\text{O}$ , gave higher total light transmissions at low filler concentrations than the best domestic carbonate, corresponding to the formula  $5\text{MgO} \cdot 4\text{CO}_2 \cdot 9\text{H}_2\text{O}$ .

7. Mixes containing between 25 and 40 per cent by weight of basic magnesium carbonate passed the greatest amount of undeviated light.

8. The amount of undeviated light passed by samples compounded with good Japanese magnesium carbonate and good domestic carbonate was essentially the same between 25 and 40 per cent filler—about 22 per cent.

9. The tensile strength of compounds containing domestic carbonate was higher in the 25 per cent filler range than that of mixtures containing Japanese carbonate.

### Acknowledgment

The authors owe special thanks to J. C. Walton and the technical staff of the Boston Woven Hose & Rubber Company for the generous use of their milling and vulcanizing equipment and for furnishing the crude rubber used. They would also like to express their appreciation to B. E. Warren, A. G. Woodman, A. C. Hardy, and associates of the Massachusetts Institute of Technology for their collaboration and valuable suggestions in obtaining the x-ray data, refractive indices, and light transmission curves. Thanks are also due to all those who so kindly furnished the samples used in this investigation.

### Literature Cited

- (1) Bratley, E. V., and Thompson, G. R., *Trans. Inst. Rubber Ind.*, **7**, 129 (1931).
- (2) Cotton, F. H., *India Rubber J.*, **77**, 867 (1929).
- (3) Dannenberg, H., *Kautschuk*, March-April, 1927, 104, 128.
- (4) Greider, H. W., *Ind. Eng. Chem.*, **14**, 385 (1922); **15**, 504 (1923).
- (5) Hardy, A. C., *J. Optical Soc. Am.*, **25**, 305 (1935).
- (6) International Critical Tables, Vol. I, p. 141, New York, McGraw-Hill Book Co., 1926.
- (7) Jones, F. C., British Patent 229,742 (1923).
- (8) Kirchhof, F., *Kautschuk*, **9**, 72 (1933).
- (9) McPherson, A. T., and Cummings, A. D., *J. Research Natl. Bur. Standards*, **14**, 535 (1935).
- (10) Menzel and Brückner, *Z. Elektrochem.*, **36**, 63, 188 (1930).
- (11) Tanaka, Y., *Trans. Inst. Rubber Ind.*, **2**, 330 (1927).
- (12) Winchel, A. N., "Microscopic Character of Artificial Minerals," p. 203, New York, John Wiley & Sons, 1931.

## "Colloidal" Zinc Oxide

H. A. Curran and T. R. Dawson

### I. Introduction

Some ten years ago, when so-called "colloidal" zinc oxides were being introduced to the rubber manufacturing industry, two samples were investigated to determine their behavior in rubber compared with ordinary good quality zinc oxide used in rubber. According to accounts published at the time, "colloidal" zinc oxide possesses an average particle size just within the limit of resolution of high-power microscopes, and an average particle diameter of 0.15 micron. In rubber it has been claimed to impart superior reinforcement, higher tensile strength, greater resistance to abrasion, and enhanced activation of organic accelerators.

In the following report, samples A and B represent two samples of the same grade of "colloidal" zinc oxide, and C a good grade of regular zinc oxide.

### Reinforcing Effects

The mixings used in this part of the work comprised a 95:5 rubber : sulfur parent stock and zinc oxide, in the proportions of 100 volumes to 20 volumes. Four stocks were prepared, containing:

- (1) "Colloidal" zinc oxide. Sample A.
- (2) "Colloidal" zinc oxide. Sample B.
- (3) "Colloidal" B and regular C in equal proportions.
- (4) Regular zinc oxide. Sample C.

New Jersey Zinc Company literature cites a mixing containing 55 per cent by weight of "Kadox" zinc oxide as vulcanizing in 45 minutes at 141° C. compared with 210 minutes for an ordinary zinc oxide. The 20-volume mixings used in the present work contained about 54 per cent by weight of zinc oxide, but preliminary vulcanizing tests did not indicate such enormous accelerating activity as that claimed above. The following table gives the properties of the rubbers at, or very near, the optimum tensile point. Vulcanization was at 60 lb. steam pressure (153° C.)

TABLE I

Test	1	2	3	4
Time of vulcanization (minutes)	50	60	60	75
Tensile strength (kg. per sq. cm.)	131	140	129	119
Elongation at break (percentage)	600	611	620	634
Elongation at 75 kg. per sq. cm. (percentage)	487	480	511	540
Rigidity (kg. per sq. cm.)	30.8	32.5	27.1	22.7
Permanent set 24 hrs. after rupture (percentage)	24.3	27.6	23.7	20.4
Permanent set after 200% elongation (percentage)	1.5	2.4	2.2	2.0
Plastometer hardness	98.5	91.5	106.0	108.5
Scleroscope resilience	70.0	64.3	69.5	68.1
Specific gravity, 15° C./4° C.	..	1.695	1.704	1.717

The tensile results in Table I and Table II, were obtained on a Schopper machine. Permanent set was measured after extension for 15 minutes at the elongation stated, followed by a recovery of 60 minutes. Plastometer hardness is the





indentation in hundredths of a millimeter of a  $\frac{1}{4}$ -inch ball under a load of 1 kilogram acting for 1 minute.

The superior reinforcing qualities claimed for the "colloidal" grade are clearly shown in these results by the increased tensile strength, toughness, and hardness. While both these samples were decidedly better in these respects than that containing the regular grade, they differed from one another somewhat.

It may be noted that the rubber containing the mixed zinc oxides (column 3) falls on the straight line joining the rubbers on either side of it (columns 2 and 4) with respect to elongation at fixed load, rigidity, permanent set, and specific gravity, but departs notably from this rectilinear relation with respect to hardness and resilience. Hysteresis as determined on a Shields rotary machine is a further property in which these zinc oxides did not satisfy the mixture law.

The finer particle size of the "colloidal" samples did not show itself in any superior covering power, and there was little choice among the four samples with respect to the whiteness of the rubber. The "colloidal" powders were, however, perceptibly more difficult to mix, with a marked tendency to cake on the rolls.

#### *Activation of Organic Accelerators.*

The mixings used in this part of the work were as follows:

(1) Smoked sheet	100 parts by weight
Sulfur	3 parts
Diphenylguanidine	1 part
Zinc oxide	3 parts
(2) Smoked sheet	100 parts by weight
Sulfur	5 parts
Hexamethylenetetramine	1 part
Zinc oxide	3 parts

In both cases, the "colloidal" sample (A) was compared with the regular product. The diphenylguanidine stocks were vulcanized at 40 lb. steam pressure ( $141^{\circ}\text{C.}$ ), and the hexamethylenetetramine stocks at 60 lb. steam pressure ( $153^{\circ}\text{C.}$ ). The general properties of these rubbers are given in Table II.

The results do not indicate any superiority of the "colloidal" product over the regular grade in activation. In the diphenylguanidine comparison the former had, on the whole, a very slight advantage; in the hexamethylenetetramine comparison a similar very small advantage was in favor of the latter product. It appears either that the sample of regular zinc oxide was an exceptionally good activator, or that the sample of "colloidal" grade did not give any special advantages in the presence of diphenylguanidine and hexamethylenetetramine.

The colors of these rubbers after equal times of vulcanization were interesting. Of the rubbers containing hexamethylenetetramine, vulcanized for 50 minutes, that with zinc oxide A was practically black, while that with zinc oxide C was very dark brown; of the rubbers containing diphenylguanidine, vulcanized for 60 minutes, that with zinc oxide A was dark brown, while that with zinc oxide C was a much lighter shade. In both stocks, therefore, the regular zinc oxide had the greater pigmenting action. Examining the samples just enumerated by transmitted light, discs 4 millimeters thick containing the regular product were quite opaque, while similar discs of the rubbers containing the "colloidal" grade allowed a perceptible amount of light to pass.

# The Oil Resistance of Rubber

## IV. Mechanism of the Oil Resistance of Neoprene

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### 1. Introduction

Though Neoprene differs chemically from natural rubber, it bears a closer physical resemblance to rubber than any of the previously known synthetic rubbers, and has a greater resistance to the action of oils than does natural rubber. To study its fine structure and the mechanism of its oil resistance is very interesting and useful for one who studies the structure of natural rubber and oil-resistant rubber. This paper describes experimental work on the dielectric properties of Neoprene and natural rubber solutions of various concentrations and viscosities, with a consideration on the mechanism of the oil-resistance of Neoprene.

### 2. Experimental

*A. Dielectric Properties of Neoprene and Natural Rubber.*—The dielectric constants of benzene solutions of Neoprene and natural rubber were measured by means of the zero beat method, using a 500 kilocycle oscillator, as detailed in the previous paper (*J. Soc. Chem. Ind., Japan*, **38**, 506B (1935)). The density, concentration, and refractive index of the solutions were determined by ordinary methods. The orientation polarizations and the dipole moments were calculated by Debye's formula. In the calculations, the molecular weight of rubber was assumed to be 544.5, as in the previous paper (*loc. cit.*). As the molecular weight of Neoprene has never been established, it was assumed that the molecular weight of Neoprene is eight times that of chloroprene, *viz.*  $[C_4H_5Cl]_8$ , or that the Neoprene molecule in a dilute solution behaves statistically in the electric field as a group of eight chloroprenes. This assumption is based only on the fact that the molecular weight of natural rubber has been assumed as eight times that of isoprene. Thus, the polarization and the dipole moments of Neoprene in this paper have only a relative meaning, rather than an absolute one. If the oil resistance of Neoprene is compared with that of natural rubber, these relative values have some significance. In the following table, the dipole moments are not calculated from the values at an infinite dilution such as  $P_{\infty,2}$ . This is based on the peculiar relation between the polarization and the concentration of Neoprene solutions. This peculiarity will be discussed in the following chapter. The Neoprene solution was prepared by shaking chips of Neoprene with purified benzene. Any purification of Neoprene, such as removing some inhibitor (Carothers, Williams, Collins, and Kirby, *J. Am. Chem. Soc.*, **33**, 4203 (1931)) was not done, because the purified Neoprene has a marked tendency to polymerize. The crude rubber-benzene solution was prepared by extracting pale crepe with benzene, as already reported (*J. Soc. Chem. Ind., Japan*, **39**, 138B (1936)). To prepare the purified rubber solution, rubber was purified as described by Pummerer (*Ber.*, **61**, 1583 (1928)). The purified rubber showed high polarization, influenced by autooxidation, as reported.

*B. Viscosity of Benzene Solutions of Neoprene and Natural Rubber.*—The viscosities of benzene solutions of Neoprene and natural rubber which were used in ob-

TABLE I  
NEOPRENE—BENZENE SOLUTION

Solution No. 107		Concentration	2.097 Wt. %			
Temp. (°C.)	Density of Solution	Dielectric Const. of Solution	$\eta_D$ of Solution	$P_{0.1}$	$\mu \times 10^{14}$	
10	0.8951	2.3767	1.5084	442.2	4.49	
20	0.8849	2.3572	1.5021	427.2	4.49	
30	0.8747	2.3342	1.4958	388.3	4.36	
40	0.8645	2.3214	1.4894	380.0	4.38	
Solution No. 105		Concentration	1.230 Wt. %			
10	0.8933	2.3425	1.5082	411.2	4.33	
20	0.8829	2.3335	1.5020	389.8	4.29	
30	0.8725	2.3163	1.4958	363.3	4.21	
40	0.8621	2.2879	1.4895	343.2	4.16	
Solution No. 109		Concentration	1.020 Wt. %			
10	0.8924	2.3349	1.5079	331.3	3.89	
20	0.8821	2.3174	1.5015	306.8	3.79	
30	0.8718	2.3003	1.4954	271.9	3.64	
40	0.8614	2.2853	1.4891	269.7	3.69	
Solution No. 108		Concentration	0.710 Wt. %			
10	0.8905	2.3186	1.5081	204.1	3.05	
20	0.8801	2.3018	1.5016	182.7	2.94	
30	0.8697	2.2847	1.4950	155.3	2.75	
40	0.8593	2.2685	1.4885	139.9	2.66	

CRUDE RUBBER—BENZENE SOLUTION

Solution No. 113		Concentration	2.742 Wt. %			
10	0.8909	2.3107	1.5083	29.1	1.15	
20	0.8805	2.2926	1.5019	22.5	1.03	
30	0.8701	2.2745	1.4955	14.4	0.84	
40	0.8597	2.2564	1.4890	7.3	0.61	
Solution No. 114		Concentration	0.911 Wt. %			
10	0.8900	2.3064	1.5082	40.9	1.36	
20	0.8797	2.2891	1.5015	35.3	1.29	
30	0.8694	2.2720	1.4949	28.4	1.18	
40	0.8591	2.2546	1.4882	21.8	1.05	

PURIFIED RUBBER—BENZENE SOLUTION

Solution No. 110		Concentration	3.924 Wt. %		
10	0.8945	2.4148	1.5079	242.3	3.33
20	0.8842	2.3918	1.5019	224.3	3.18
30	0.8739	2.3710	1.4959	210.2	3.20
40	0.8636	2.3475	1.4898	191.1	3.10
Solution No. 115		Concentration	3.036 Wt. %		
10	0.8935	2.3799	1.5081	249.4	3.37
20	0.8832	2.3571	1.5019	230.9	3.30
30	0.8729	2.3344	1.4956	210.7	3.21
40	0.8626	2.3116	1.4895	189.5	3.09
Solution No. 111		Concentration	1.022 Wt. %		
10	0.8908	2.3356	1.5082	315.3	3.79
20	0.8805	2.3151	1.5018	278.8	3.63
30	0.8703	2.2943	1.4954	234.1	3.38
40	0.8600	2.2736	1.4889	191.7	3.11

serving dielectric properties were measured in an Ostwald viscometer (capillary bore 0.7 mm. and length 150 mm.) in a water thermostat at 20°C. In the following table,  $\eta_{sp}$  is the specific viscosity defined by:  $\eta_{sp} = \eta_{rel} - 1$ , in which  $\eta_{rel}$  is the relative viscosity of the solution (based on that of the solvent),  $C$  is the concentra-

tion in grams of solute in 100 cc. of solution,  $f$  is the specific volume (cf. Mark and Fikentscher, *Kolloid Z.*, **49**, 135 (1929)). The relations between  $\eta_{sp}/C$  and the concentration are shown in Fig. 1.

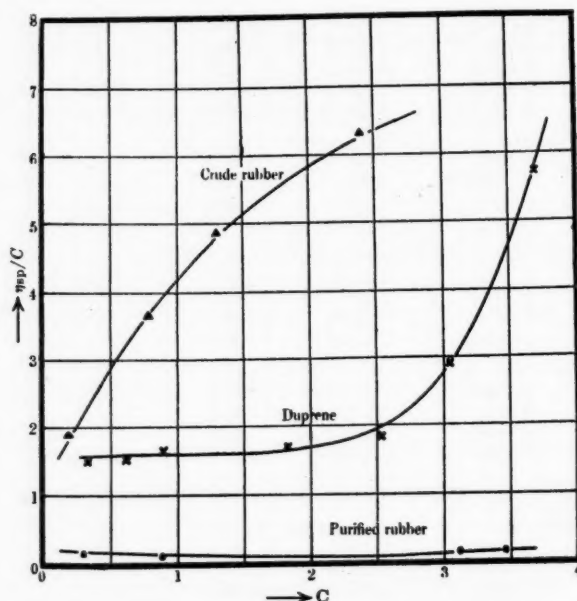


Figure 1

TABLE II

Solute	No. of Solution	$C$	$\eta_{sp}$	$\eta_{sp}/C$	$f$
Neoprene	112	0.314	0.453	1.445	48.9
	108	0.625	0.922	1.476	43.1
	109	0.900	1.460	1.623	41.0
	107	1.856	3.215	1.732	30.3
	118	2.540	4.615	1.817	25.5
	117	3.059	8.767	2.866	25.4
	121	3.700	21.182	5.725	24.2
Crude rubber	119	0.192	0.365	1.902	66.4
	114	0.801	2.953	3.687	67.6
	116	1.332	6.493	4.875	54.2
	113	2.413	15.137	6.270	35.6
	122	2.041	13.943	6.831	17.5
Purified rubber	111	0.900	0.087	0.096	3.7
	115	2.661	0.273	0.102	3.7
	110	3.470	0.397	0.114	4.0

### 3. Discussion

The above results can be summarized as follows.

A. Neoprene shows a far higher polarization than does crude natural rubber. This may be the chief cause of the oil-resistance of Neoprene.

B. The polarization of Neoprene is of the same order of magnitude as that of purified rubber which is influenced by autooxidation.

C. Increase in the concentration of Neoprene solution increases the polarization of Neoprene, whereas increase in the concentration of natural rubber solutions decreases the polarization, as shown in Fig. 2. The relation between the polarization and the concentration is affected by the association of solute. There are two possible simple forms of association, as shown in Fig. 3 by A and B. If a polar solute associates as type A in a non-polar solvent, the polarization becomes higher in more dilute solution; while the solute has a tendency to associate as type B, polarization increases with increase in concentration. This theory may be applied to the results above. Neoprene seems to associate as type B, natural rubber as

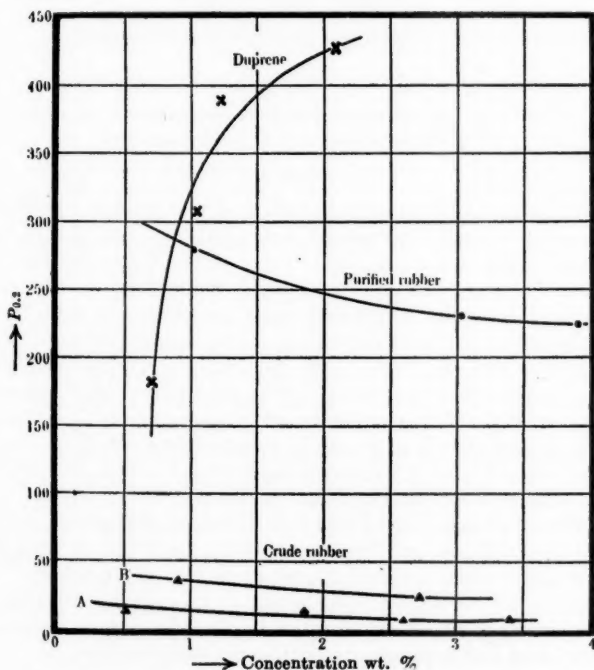


Figure 2—A: Observed Data on a Crude Rubber Solution in October, 1935  
B: Observed Data in March, 1936 on the Same Solution, Which Was Stored in a Glass-Stoppered Bottle in a Dark Room

type A. This tendency of Neoprene probably promotes polarization more and more with the increase in concentration. As the final state, the gel forms of Neoprene and its  $\mu$ -type polymer may be such highly polar substances that they become only slightly swollen by non-polar solvents and mineral oil.

D. The expression,  $\eta_{sp}/C$ , means the molecular weight of solute or the chain-length of the molecule, according to the viscosity theory of Staudinger ("Die hochmolekularen organischen Verbindungen, 1932;" Staudinger, *Trans. Inst. Rubber Ind.*, 10, 263 (1934)). The  $\eta_{sp}/C$  of crude rubber shows a steep ascent with increase of concentration  $C$ , while the value of Neoprene increases gradually at first, and the value of purified rubber remains almost constant, regardless of the concentration. It is very interesting that the shape of the curves of  $\eta_{sp}/C$  to  $C$  of Neoprene and crude rubber are almost the reverse of those of polarization and concentration,

as shown in Figs. 1 and 2. If the polar molecules associate as type B in Fig. 3, and the associated molecule behaves as a rod the length of which is shown by  $\eta_{sp}/C$ , the curve of  $\eta_{sp}/C$  to  $C$  of Neoprene should become similar to the polarization-concentration curve. The contrary experimental results can be explained as follows. The viscosity of a solution does not depend only on the chain-length of the solute, but also is affected by the degree of solvation, which is much influenced by the polarization of the solute. At the same time, the associated molecule of Neoprene does not behave as a rod, but can bend freely. The bent molecule occludes me-

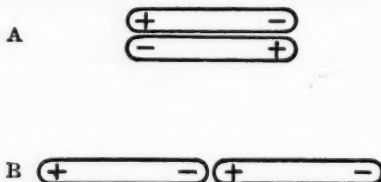


Figure 3

chanically some solvent. This immobilization of the solvent results in a distinct increase of the viscosity with increase of concentration. Increase of concentration chiefly increases the polarization, and this disturbs the solvation of non-polar solvents such as benzene. In accordance with the increase in concentration, the associated molecule becomes longer and longer, and tends to bend freely. Haller reported that long molecules are more likely to bend markedly from the viewpoint of the Raman spectrum (*Kolloid. Z.*, **56**, 257 (1931)). This bending reduces the increase of the polarization, and brings about immobilization of the solvent, which increases the viscosity. This may be because the curve of Neoprene in Fig. 1 is the reverse of the curve in Fig. 2. In the case of crude rubber, the molecule is non-polar, and has a tendency to associate, as type A in Fig. 3. This molecule is very likely to solvate in sufficiently dilute solutions. As shown in Fig. 1, purified rubber is so severely disaggregated that it is dissolved almost in a molecular state, and its  $\eta_{sp}/C$  does not depend on the concentration; nevertheless the polarization of purified rubber is of the same order of magnitude as that of Neoprene.

Thus, Neoprene has as high a polarization as has purified rubber, and also as complex a gel structure as has crude rubber. For this reason, Neoprene shows a high oil-resistance and a fair tensile strength in the swollen state.

#### 4. Summary

To study the mechanism of the oil resistance of Neoprene, the following points were investigated.

1. The dielectric properties of Neoprene and its comparison with the crude and purified natural rubber.
2. The viscosity of benzene solutions of Neoprene and natural rubber of various concentrations.

From data on the relation between polarization, the chain-length of solute and the concentration, the state of solutes in solution was discussed, and the oil resistance of Neoprene is explained on the basis of its high polarization and its complex structure.

In conclusion, the author wishes to express his thanks to Professor Yoshio Tanaka for valuable suggestions and criticisms.

[NOTE.—On Figs. 1 and 2, the expression "Duprene" appears. This is the former term for "Neoprene," and represents the same substance.]



# Impact Machine for Rubber Testing

## Determining the Stress-Strain Diagram at High Speed

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**I**N CONTRAST to the ordinary standard procedure at low speed, various methods have been devised to carry out tensile tests of rubber under rapid application of load, with the purpose of securing more definite indications, at a speed in agreement with actual performance. The application of those methods to the study of the tensile properties of rubber stocks goes as far back as 1910, when Beadle and Stevens (1) made use of the pendulum to investigate these properties. Their work applied to rubber compounds of different compositions and different loadings.

More recently, Van Rossem and Beverdam (2) presented a set of results tending to prove an optimum in the tensile properties, coinciding with the best cure as determined by practical observation.

However, all experiments, previous to those here reported, are limited to the determination of the tensile strength of rubber, and no attempt was made to extend the investigations to the determination of the resistance of rubber at different elongations.

The machine here illustrated is designed to measure not only the energy absorbed at break, under conditions of high speed, by impact, but also the stress-strain relation.

### General Features

Figure 1 shows a general view of the impact tester as designed by the author and in use at the Goodyear Research Laboratories. The pendulum hammer and the test piece are in position ready for test. Figure 2 represents a close view of the pendulum hammer and scales.

**ELONGATION FEATURES.** The most important parts of the elongation system are the tripping device and the arcuated member secured to the pendulum hammer.

The method of securing the test piece to the machine consists in having one of the two supporting pins capable of dropping from position whenever the lock is set free by the impact of the elongation pin secured at the arcuated member of the pendulum hammer. The dropping pin supporting one end of the test piece is carried by a cylinder capable of rotating around a pinion.

The method of arresting and releasing the rotor is illustrated by the detailed view of the tripping device (Figure 3).

To secure the release of the test piece at different elongations, an arc is attached to the pendulum hammer. To this arc is secured a removable pin, capable of releasing the tripping device at any prefixed elongation of the test piece. The arc carries a series of holes at such distances as to operate at zero elongation, at 50, 100, 150, and every 50 per cent elongation up to 400 per cent. On the present machine, holes are also provided for 10, 20, 30, 40 per cent, and also for 450 up to 650.

Experimental determinations, carried out by the use of fine metallic wire of proper lengths secured with the rubber test piece in proper position for test, tend to demonstrate that the test piece is fully released at the elongation required.

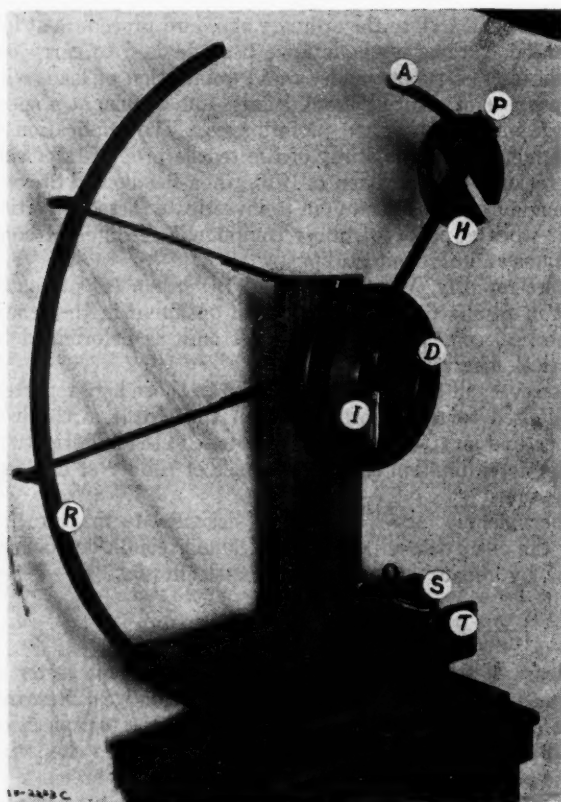
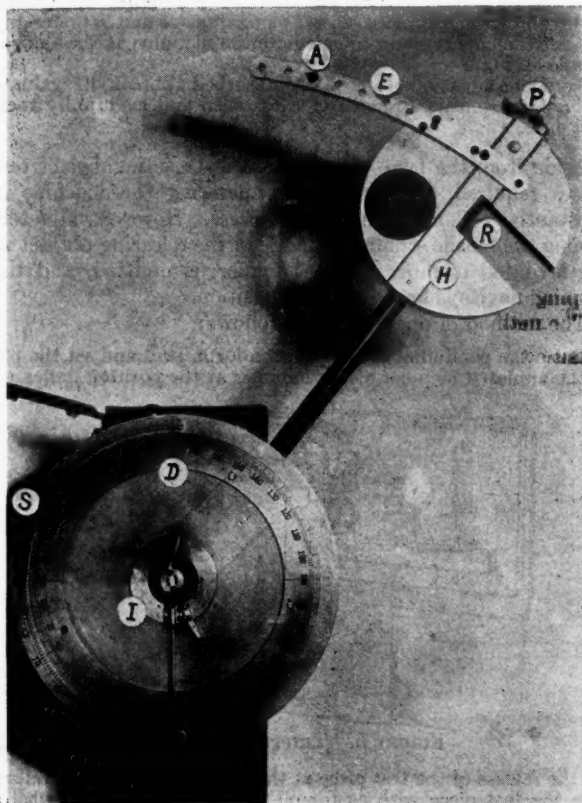


FIGURE 1. GENERAL VIEW OF MACHINE

- A. Arcuated member on which are directly indicated settings of pin used to trip releasing device at different elongations of test piece
- D. Dials
- H. Pendulum hammer
- I. Indicator
- P, R. Pawl and rack arrangement (used only for special purposes, pawls being normally kept in a lifted position)
- S. Pins securing test piece at proper position
- T. Support, at back of which is secured the tripping mechanism

In Figure 3 the arrows indicate the direction of the motions and illustrate the coördination of the movement of the arcuated member, with the release of the trigger.

**TEST PIECE.** Although different experiments were carried out, using the dumbbell test piece, the ring type was finally adopted for convenience. The rings are cut from the ordinary



**FIGURE 2. CLOSE VIEW OF PENDULUM HAMMER AND SCALES**

- A. Arcuated member attached to pendulum hammer
- D. Degree scale (divided in tenths)
- E. Openings for holding releasing pin at different elongation settings
- H. Pendulum hammer
- I. Indicator arrangement and sliding supporting disk, pressed (at back) by a series of small springs
- P. Pawls, with small adjusting cam
- R. Roller at center of pendulum hammer, against which stretches central portion of lubricated test piece while pendulum advances
- S. Scale for corrected readings of available kinetic energy of pendulum

molded 2-mm. sheets, by the same procedure used for the dumbbell test piece. The diameter, measured at the middle of the width, is 7.0 cm.; the initial length is 11 cm. (half of the circumference). Figure 4 shows the three test pieces (6.3, 5, and 3 mm. in width) and the corresponding dies.

### Operation

The procedure to be followed in the operation of the machine can be considered in three ways:

1. Procedure required to obtain the maximum of accuracy necessary to calculate the full extent of the stress-strain curves. A new test piece is required for the determination of each point.
2. Simplified procedure sufficient to determine the energy absorbed by the test pieces at two elongations,  $a$  and  $b$  (preferably 100 per cent apart), and to calculate the modulus at the elongation  $(a + b)/2$ .
3. Determination of the energy absorbed at break, to evaluate the relative tensile strength of the stocks and eventually their best cure.

Aside from the type of correction and the number of test pieces required, the method of operating the machine is substantially identical in all three cases. However, in determining the tensile strength, the use of the releasing pin, set at the arcuated member of the hammer, is omitted, and the tripping device is kept in locked position.

The method of operation is as follows:

Raise the pendulum to the position for impact and set the pin in the arcuated member of the hammer at the position indicated

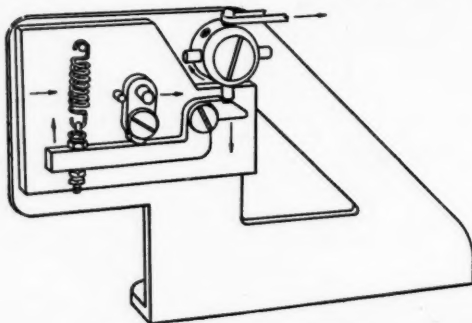


FIGURE 3. TRIPPING DEVICE

for the release of the test piece at the elongation wanted. Lubricate the test piece with castor oil, or castor oil diluted with a mixture of methanol and ether. Set the ring test piece, across the pendulum path, from the movable to the stationary pin and lock the trigger of the tripping device. Release the pendulum weight and record the readings of the dials.

In operating the machine, the pendulum ruptures or carries the test pieces to a definite elongation when near or at the bottom of the fall.

The difference between point  $H$ , from which the center of gravity of the pendulum is allowed to drop, and height  $H_1$ , to which it rises at the other side of the stroke, is proportional to the energy required to break or to elongate the test piece. The energy absorbed is equal to:

$$W(H - H_1)$$

where  $W$  = weight of the pendulum

### Construction Details and Calculation of Results

The total drop height and available drop heights of the pendulum hammer when due allowance is made for frictional resistances are:

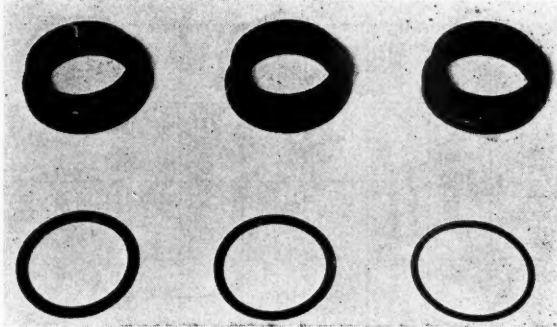


FIGURE 4. TEST PIECES AND DIES

Distance of the center of gravity from the axis of rotation, 56.6 cm.

Maximum pendulum deviation from the vertical,  $142.3^\circ$ ; total drop height, 101 cm.

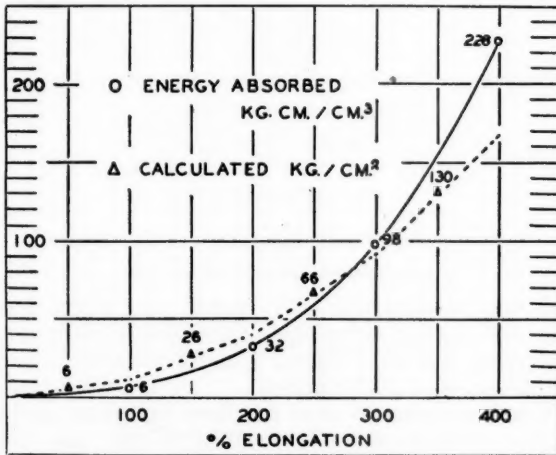


FIGURE 5. CALCULATION OF KG. PER SQ. CM. VALUES FROM ENERGY ABSORBED (KG. CM. PER CC.)

Available drop height when correction is made for bearing and air resistance and for frictional resistance of the pointer, 100 cm.

Available drop height when further correction is made for the resistance due to the tripping device, 98.5 cm.

On the dial for the direct reading of the per cent energy absorbed, when the elongation device is used, the graduation

of the scale represents the drop in centimeters of the center of gravity of the hammer from 98.5 cm. above its lowest position.

Hammers of different weights were adopted on account of wide differences in resistance of the rubber stocks. The

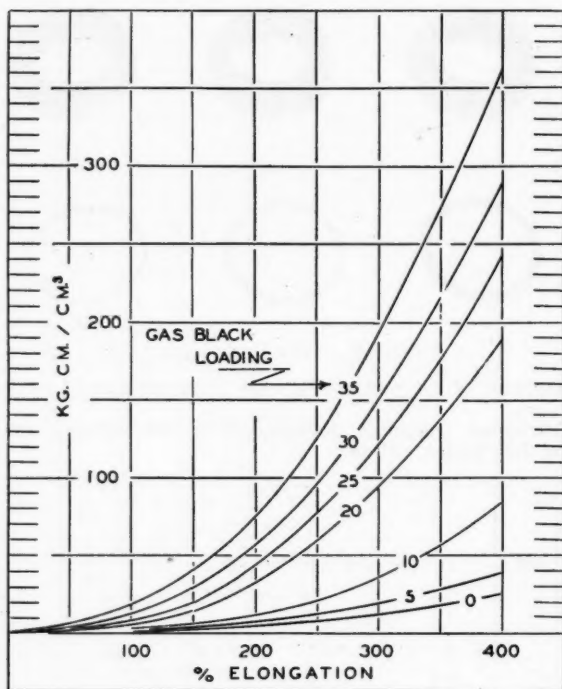


FIGURE 6. ENERGY ABSORBED AT LOW SPEED  
50 cm. per minute, by usual methods

three weights used are 4,077, 10,695, and 13,325 grams. They are quickly interchangeable, being constructed of overlapping sections. Figures 1 and 2 illustrate a single-weight hammer of 10,695 grams.

The average dimensions of the three test pieces used are as follows: mean diameter of all three ring-test pieces, 7.0 cm.; widths, 6.3, 5.0, and 3.0 mm.; volume per millimeter of thickness, 1.38, 1.08, 0.65 cc., respectively; average gage, 1.8 mm.

The factors for the calculation of the energy absorbed per unit volume of the test piece, from calculations are as follows:

Test Piece (1.8-Mm. Gage)	Width Mm.	Vol. Cc.	Factors for:		
			74.08-kg. wt.	10.69-kg. wt.	13.3-kg. wt.
			Kg. cm. per cc.		
	6.3	2.49	1.61	4.23	5.26
	5.0	1.95	2.06	5.40	6.72
	3.0	1.17	3.43	9.00	11.20



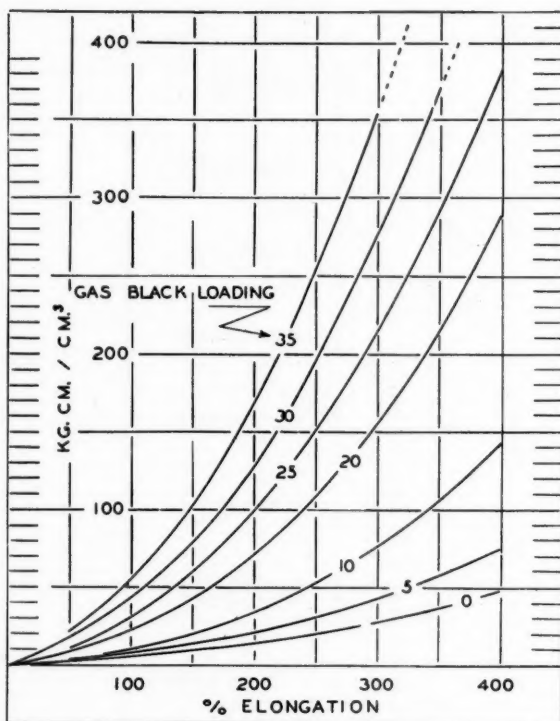


FIGURE 7. ENERGY ABSORBED AT HIGH SPEED BY IMPACT  
25,000 cm. per minute

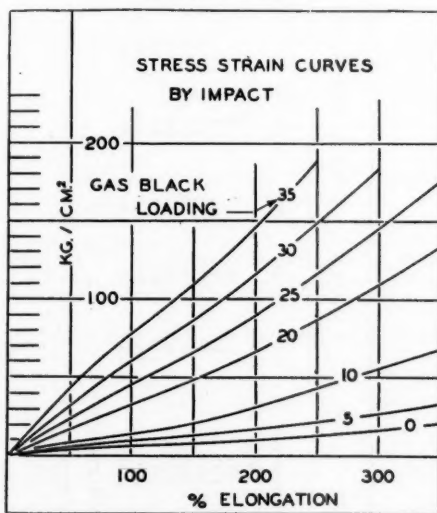


FIGURE 8. STRESS-STRAIN RELATIONSHIP BY  
IMPACT  
Kg. per sq. cm. calculated from kg. cm. per cc. values



The factors, based on the equivalence of results, from experimental data are:

Test Piece (1.8-Mm. Gage) Width Mm.	Vol. Cc.	Factors for:		
		4.08-kg. wt.	10.69-kg. wt.	13.3-kg. wt.
6.3	2.49	1.7	4.23	5.2
5.0	1.95	2.0	5.3	6.5
3.0	1.17	3.3	8.7	10.8

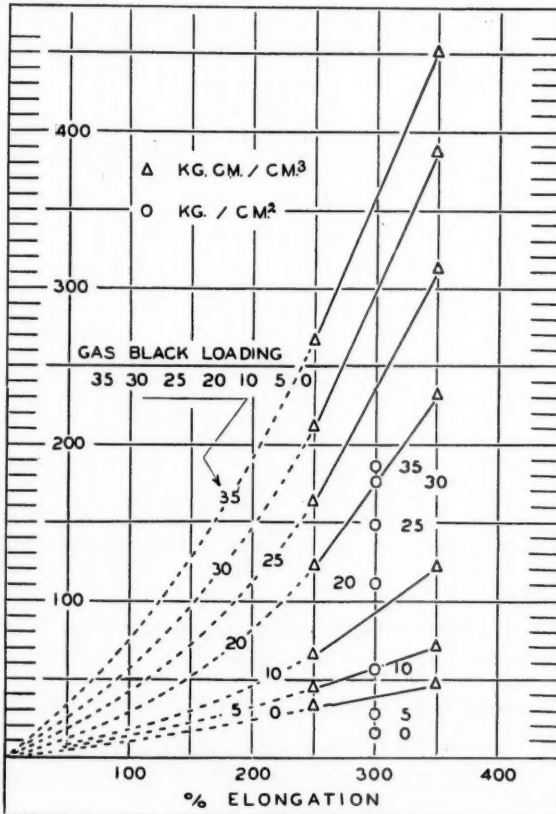


FIGURE 9. ENERGY ABSORBED BY IMPACT

At 250 and 350 per cent elongation and calculated modulus at 300

The actual drop height of the hammer at different elongations is:

Elonga- tion %	Drop Height Cm.	Elonga- tion %	Drop Height Cm.	Elonga- tion %	Drop Height Cm.
20	95.2	300	99.8	500	96.2
100	98.9	400	98.4	600	94.9
200	98.1				

For ordinary determinations, this correction is generally not required but was applied in calculating the results illustrated here.

The correction for frictional resistance of the test piece, at the pins, was calculated as the energy absorbed at no elongation by releasing the tripping device at such position, and recording the energy absorbed. This determination is desirable to establish the operating condition of the machine and the characteristics of the stock tested. The values range between 5 and 7 kg. cm. per cc., according to the type of stock. The results are very uniform when the test piece is previously lubricated, as indicated under "Operation."

The striking velocity of the pendulum hammer is calculated from the equation

$$V = \sqrt{2GS}$$

where  $V$  = velocity at end of time  $t$ , sec.  
 $S$  = vertical space traversed in time  $t$  (100 cm.)  
 $G$  = acceleration of gravity (980)  
 $V = \sqrt{2 \times 980 \times 100}$   
 = 443 cm. per sec.  
 = 26,580 cm. per min.  
 = 10 miles per hour

The calculation of the stress-strain curves (in kg. per sq. cm.) from the relation between elongation and energy absorbed (in kg. cm. per cc.) is made as follows:

The area under the stress-strain curves can, with sufficient degree of approximation, be divided into a series of trapeziums.

The number of kg. per sq. cm. at  $E$  per cent elongation = [(kg. cm./cc. at elongation  $E + A$ ) - (kg. cm./cc. at elongation  $E - A$ )] multiplied by  $100/2A$ .

The area under the curve representing kg. cm. per cc. between 0 and 50 per cent elongation can be considered as a triangle. The number of kg. per sq. cm. at 25 per cent elongation can be considered equal to the number of kg. cm. per cc. at 50 per cent elongation.

Figure 5 illustrates graphically the procedure used to calculate the stress-strain curve from the values of kg. cm. per cc.

### Experimental Applications to Vulcanized Rubber

The following is a series of tests applied to vulcanized rubber. No attempt is made to illustrate the application of the machine to uncured stock.

**COMPOSITION AND CURE.** The composition of the stocks tested was as follows:

Stock No.	V-92	V-93	V-94	V-95	V-96	V-97	V-98
Rubber	100	100	100	100	100	100	100
Gas black	None	9.4	18.8	37.5	47.1	56.4	65.8
Zinc oxide	5	5	5	5	5	5	5
Sulfur	3	3	3	3	3	3	3
Stearic acid	4	4	4	4	4	4	4
Captax (mercaptobenzo-thiasole)	0.35	0.50	0.80	1.2	1.3	1.3	1.3
Vol. gas black loading	0	5	10	20	25	30	35

Cures were 35, 50, 70, 100, and 140 minutes at 260° F. The best cure, as judged by tear and practical observation,

was 70 minutes. Therefore, in the following tests (except for the application of the impact test to the determination of the best cure), only the 70-minute cure was represented.

**ELONGATION AND ENERGY ABSORBED.** The relation between elongation and energy absorbed at low speed by the usual methods and at high speed by impact is shown in Figures 6 and 7. The comparison between energy storage capacity at 50 and at 25,000 cm. per minute is given in Table I.

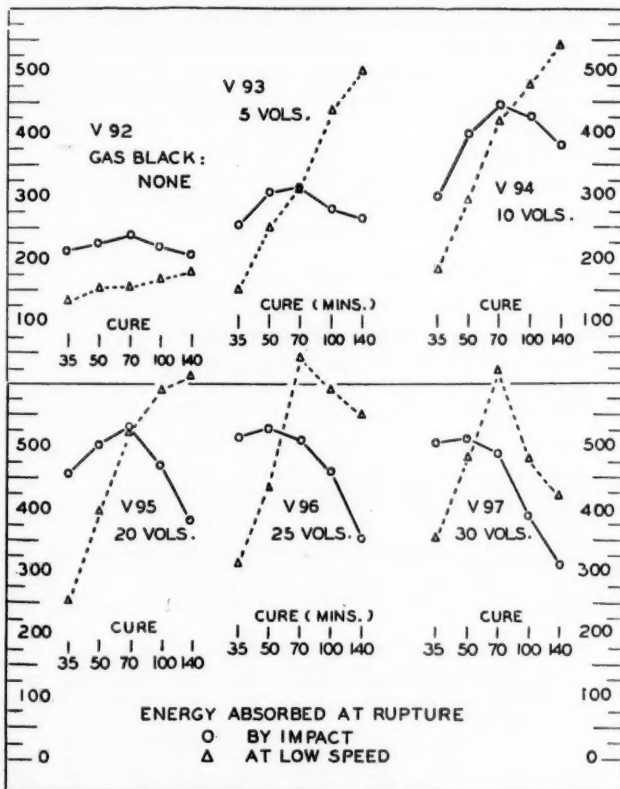


FIGURE 10. ENERGY ABSORBED AT RUPTURE, IN RELATION TO CURE

**STRESS-STRAIN DATA.** The stress-strain curves by impact, calculated from the relation between elongation and energy absorbed, are given in Figure 8. The stress-strain data calculated from Table I are as follows:

Elongation %	Gas Black Content, Volumes:						
	0	5	10	20	25	30	35
	Kg. per sq. cm.						
25	3	4	6	8	13	17	24
100	7	10	14	34	45	62	79
150	8	12	22	48	66	85	109
200	11	17	32	66	91	117	147
250	13	22	42	86	116	150	188
300	15	27	56	109	147	174	...
350	21	33	68	134	170	...	...

**SIMPLIFIED DETERMINATION OF ENERGY ABSORPTION AND MODULUS.** A simplified procedure limited to the determination of the energy storage capacity at 250 and 350 per cent elongation and to modulus at 300 per cent is shown in Figure 9 and in Table II.

**ENERGY ABSORPTION AT BREAK.** The energy storage capacity at break in relation to best cure is shown in Figure 10.

Probably one of the most useful applications of the impact test is the determination of the best cure, from the standpoint of energy storage capacity. The difference between cure is, in some cases, not very accentuated and almost on the limit of the errors involved in the test. However, the general trend is, in most cases, sufficient to indicate the true value of the best cure.

TABLE II

Elongation %	Gas Black Content of Stock, Volumes:						
	None	5	10	20	25	30	35
350	11.3 <sup>a</sup>	16.9 <sup>a</sup>	28.8 <sup>a</sup>	55.3 <sup>a</sup>	58.8 <sup>a</sup>	44.5 <sup>a</sup>	(52) <sup>a</sup>
250	7.7 <sup>a</sup>	10.4 <sup>a</sup>	15.4 <sup>a</sup>	29.0 <sup>a</sup>	30.9 <sup>a</sup>	24.4 <sup>a</sup>	30.7 <sup>a</sup>
Test Piece Width, Mm.:							
	6.3		5		3		
Experimental Factors							
	4.2		5.3		8.7		
	Energy Storage Capacity						
350	47 <sup>b</sup>	71 <sup>b</sup>	121 <sup>b</sup>	232 <sup>b</sup>	312 <sup>b</sup>	387 <sup>b</sup>	(452) <sup>b</sup>
250	32 <sup>b</sup>	44 <sup>b</sup>	65 <sup>b</sup>	122 <sup>b</sup>	164 <sup>b</sup>	212 <sup>b</sup>	267 <sup>b</sup>
	Modulus						
300	15 <sup>c</sup>	27 <sup>c</sup>	56 <sup>c</sup>	110 <sup>c</sup>	148 <sup>c</sup>	175 <sup>c</sup>	185 <sup>c</sup>

<sup>a</sup> Scale reading (per cent energy absorbed).

<sup>b</sup> Values marked <sup>a</sup> multiplied by the corresponding factors.

<sup>c</sup> Modulus (kg. per sq. cm.), calculated from values marked <sup>b</sup>.

Following is a comparison of results obtained at 50 cm. per minute with those at more than 25,000 cm. by impact; the cures were 35, 50, 70, 100, and 140 minutes at 260° F.:

Stock No.	Gas Black Loading Vol.	Ratings in % of Lowest Cure Values							
		At low speed				By impact			
		50- min.	70- min.	100- min.	140- min.	50- min.	70- min.	100- min.	140- min.
V-92	None	116	118	128	132	108	113	106	101
93	5	169	228	295	340	118	123	110	104
94	10	163	234	267	297	132	152	146	126
95	20	157	207	237	243	110	116	104	83
96	25	140	206	192	178	104	99	90	68
97	30	131	178	138	119	100	98	77	62
98	35	128	147	128	112	99	97	75	47

### Acknowledgment

The author desires to express his thanks to R. P. Dinsmore and L. B. Sebrell for permission to publish this paper, and to W. W. Vogt and M. J. DeFrance for valuable criticism.

### Literature Cited

- (1) Beadle, C., and Stevens, H. P., *Proc. Intern. Rubber Congr. London*, 1911, pp. 344-50.
- (2) Van Rossem, A., and Beverdam, H. B., *Rubber Chem. Tech.*, 4, 147-55 (1931).



# Vulcanization Characteristics of Mercaptobenzothiazole Derivatives

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**W**ITHIN the past few years much progress has been made in the development of rubber vulcanization accelerators of the semi-ultra type which exhibit no prevulcanization or scorch during the preliminary processing. Most of the commercially important members of this class are derivatives of mercaptobenzothiazole in which the hydrogen atom of the mercapto group is replaced by an organic substituent. The increasing use of these products can be attributed to their favorable curing characteristics and to the valuable physical properties which they impart to the cured stock. Naunton and his co-workers (4), Twiss and Jones (8), and Shepard (6) discussed a number of these compounds in recent papers. Numerous references to their preparation and use also appear in the patent literature (1,2,3,5,7, 10).

The purpose of this paper is to determine the effect of various substituents upon the curing value and scorching tendency of mercaptobenzothiazole condensation derivatives. Few of these materials exhibit the desired curing action when used alone; some are activated more or less by diphenylguani-

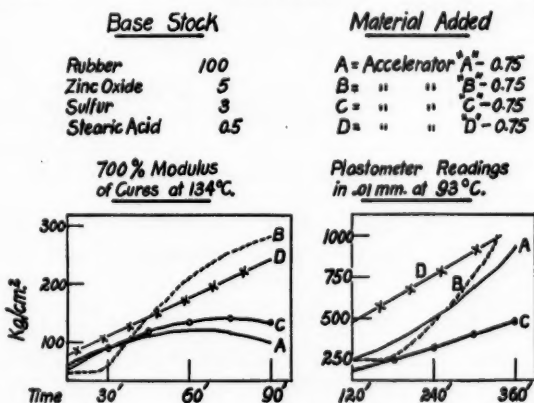


FIGURE 1

dine; others remain unaffected. Primarily, the compounds of interest are those which alone or activated are stronger

but less scorchy accelerators than mercaptobenzothiazole. However, certain ones which are strongly activated by diphenylguanidine and thereby show a moderate scorching tendency should not be overlooked since in many cases it is possible to eliminate prevulcanization by substituting a retarding activator such as diphenylguanidine phthalate. It is also recognized that a complete compounding study is necessary for the proper evaluation of any accelerator.

### Experimental Procedure

In order to obtain a first approximation of the vulcanization characteristics and possibilities of these materials, they

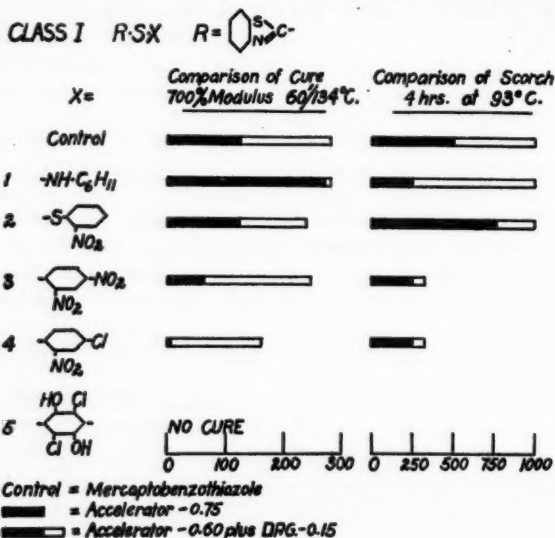


FIGURE 2

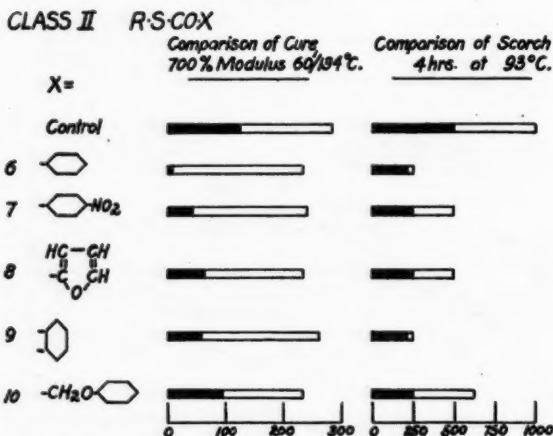


FIGURE 3

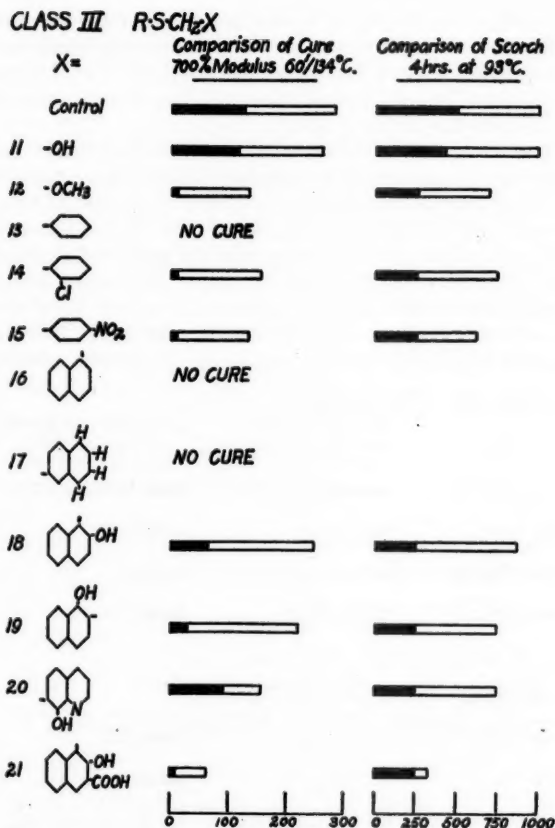


FIGURE 4

were compared alone and activated by diphenylguanidine, using mercaptobenzothiazole as a control. The general test recipe is shown in Figure 1, along with several typical modulus and plastometer curves obtained from representative accelerators of this class. The 700 per cent modulus figures (in kg. per sq. cm.) of the 60-minute cures at 134° C. were chosen to express the acceleration value, and the Williams plastometer readings (9), obtained after heating pellets of the uncured stock for 4 hours at 93° C., were selected to represent the degree of scorch. A plastometer reading of 250 is equivalent to no scorch, inasmuch as a gum stock compounded without an accelerator will give this figure; the scorching tendency is indicated by the magnitude of the higher readings. Curve A represents mercaptobenzothiazole; B, C, and D represent various mercaptobenzothiazole derivatives activated by diphenylguanidine.

Curve B displays the definite lag or induction period both in cure and scorch characteristic of true delayed action ac-

celeration. Accelerator C is similar to A in cure but much less scorchy. D is an example of a strong scorchy accelerator. From a comparison of these modulus and plastometer curves, it is evident that the curing value and the amount of scorch are independent of one another.

The mercaptobenzothiazole derivatives which follow have been classified according to certain similarities in structure. As far as possible, each class contains compounds with a common substituent grouping attached to the thiol sulfur. Their curing and scorching properties are represented graphically by means of rectangular strips; the solid portion indicates the results obtained when 0.75 part of the derivative are added to the base stock; the entire strip, including the solid and blank portions indicates the results obtained

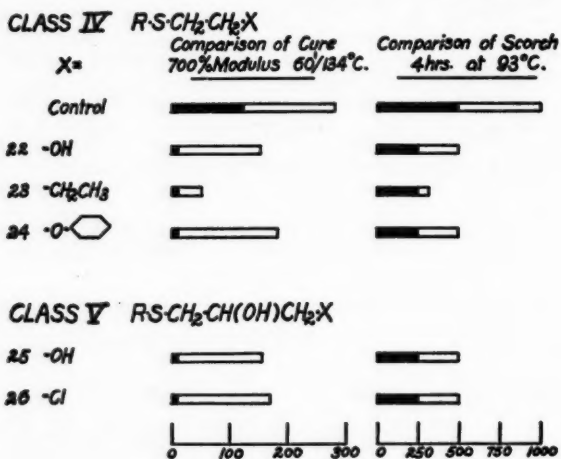


FIGURE 5

when 0.60 part of the derivative plus 0.15 part of diphenylguanidine are used.

### Discussion

**CLASS I.** Compounds 1, 3, and 4 (Figure 2) exhibit the most desirable properties. Compound 1 is rather exceptional in that alone it is quite a rapid, high-modulus, nonscorchy accelerator. In this case activation is not necessary nor is it desirable. Compounds 3 and 4 alone have little or no curing action but, upon activation, surpass unactivated mercaptobenzothiazole and show substantially no scorch. Compound 2 alone is more scorchy than the control, and compound 5 shows no cure. The latter is the first example of a non-accelerator which has negative groups present in the substituent.

**CLASS II.** The members of this class (Figure 3) show little acceleration alone but are strongly activated; compounds 6 and 9 are most interesting since they are not scorchy but

yet give high-modulus cures. Compounds 7 and 8 when activated have a scorching tendency about equal to unactivated mercaptobenzothiazole; that of compound 10 is somewhat greater.

CLASS III. Compound 11 (Figure 4) is similar to the control in its properties, both alone and activated. Compounds 12, 14, 15, 18, 19, and 20 upon activation give a cure equal to or better than unactivated mercaptobenzothiazole, but have a much greater scorching tendency. Compounds 13, 16, 17, and 21 show little or no acceleration value, either alone or with diphenylguanidine. Compounds 13, 16, and 17 are derivatives containing nonpolar constituents and display the inertness characteristic of this type. Compound 21 is the second example of a nonaccelerator containing negative groups, the carboxyl group evidently nullifying the effect of the hydroxyl group which was manifest in the three preceding compounds.

CLASSES IV AND V. With the exception of compound 23 (Figure 5) which shows the inactivity typical of straight-chain hydrocarbon substitution, the members of these classes when activated have a greater acceleration value than unactivated mercaptobenzothiazole and about the same scorch.

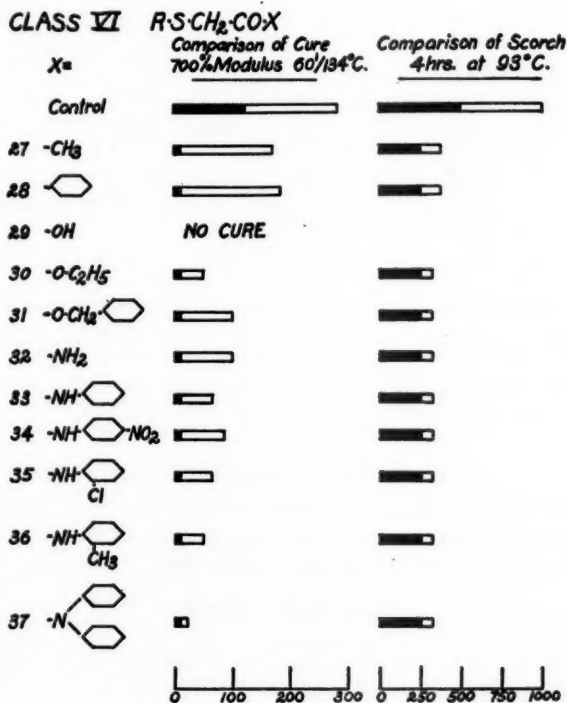


FIGURE 6

## CLASS VII RSXSR

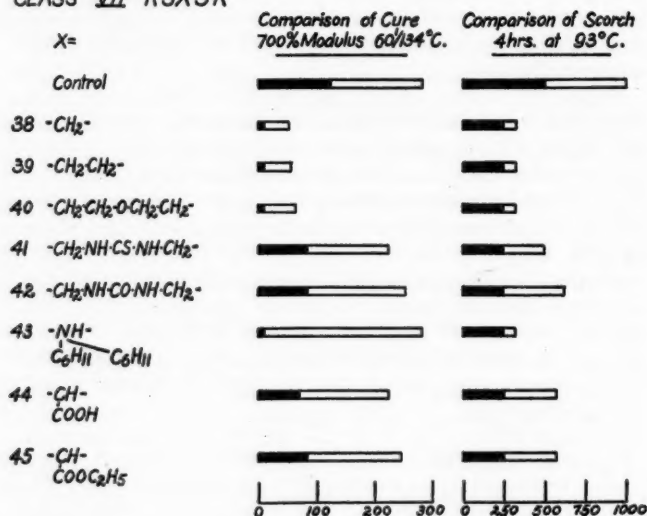


FIGURE 7

CLASS VI. Compounds 27 and 28 (Figure 6) upon activation show greater acceleration value and less scorch than unactivated mercaptobenzothiazole. The other members of this class are of no particular value; 29 and 30 are further examples of inactive compounds which contain negative groups; 32 to 37, inclusive, which were prepared by reacting mercaptobenzothiazole with various substituted acetamides, might be considered along with 29 and 30; however, the net negative effects of their substituents are so extremely weak that they seem to exert little or no effect.

CLASS VII. In agreement with four previous examples, compounds 38, 39, and 40 (Figure 7) show the inertness characteristic of nonpolar substituents. The other members of this class are strongly activated. Compounds 41, 42, 44, and 45 show a scorching tendency equal to or greater than unactivated mercaptobenzothiazole; compound 43 shows the highest acceleration value and the least scorch.

### Acknowledgment

The author wishes to thank E. W. Booth for his assistance in assembling the vulcanization data given, and the research staff of this laboratory for helpful suggestions.

### Literature Cited

- (1) Evans, U. S. Patent 2,020,051 (1935).
- (2) Harman, *Ibid.*, 1,951,052 (1934); 2,010,000 (1935).
- (3) Horst, W. P. ter, U. S. Patent 1,941,142 (1933).
- (4) Naunton, W. J. S., Baird, W., and Bunbury, H. M., *J. Soc. Chem. Ind.*, **53**, 127 (1934); *Rubber Chem. Tech.*, **7**, 417 (1934).



- (5) Scott, U. S. Patents 1,732,486 (1929); 1,784,498 (1930); 1,965,160 (1934).
- (6) Shepard, N. A., *Ind. Eng. Chem.*, 28, 281 (1936).
- (7) Sibley, U. S. Patent 1,936,099 (1933).
- (8) Twiss, D. F., and Jones, F. A., *J. Soc. Chem. Ind.*, 54, 13 (1935);  
*Rubber Chem. Tech.*, 8, 230 (1935).
- (9) Williams, I., *Ind. Eng. Chem.*, 16, 362 (1924).
- (10) Zimmermann, U. S. Patent 1,960,197 (1934).

# Soft Vulcanized Rubber

## Effect of Temperature and Oxygen Pressure on Aging Rate

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**I**MPORTANT to the manufacturer and consumer of rubber goods are suitable accelerated aging tests for predicting readily the life of rubber articles under the variable storage and service conditions encountered. Since service conditions may involve the exposure of rubber to wide variations of temperature, light, and atmosphere under various types of mechanical strain, there is obviously need for a variety of tests, each designed to emphasize factors which are most important in any given set of service conditions.

Since the primary cause of failure of soft vulcanized rubber in service is oxidation, emphasis has been placed on tests which accelerate the oxidation effect. The most widely adopted and generally satisfactory procedure of this type is the Bierer and Davis oxygen bomb method which involves heating the rubber under oxygen pressure.

In Bierer and Davis' original publication (2), results were shown on the effect of increasing oxygen pressure in increments of 28.1 kg. up to 112.5 kg. per cm. on the aging of two different rubber compounds at the three temperatures, 50°, 60°, and 70° C. Their results showed that in some cases there was a uniform increase in aging rate with increased pressure and in other cases the rate increased rapidly up to a pressure of 28.7 kg. per sq. cm. but more slowly with further increases in pressure. In a later investigation (3) the same authors employed a pressure of 21.1 kg. per sq. cm. and 60° C. throughout. For the past ten years most laboratories have used an oxygen pressure of 21.1 kg. per sq. cm. and a temperature of 70° C., which may therefore be considered as standard.

No data have been found in the literature to show the effect on the aging rate at 70° C. of increasing the oxygen pressure in smaller increments up to 21.1 kg. per sq. cm. Williams and Neal (4) studied the effect of bomb aging at 50° C. on a soft vulcanized rubber compound containing 90 per cent rubber and 10 per cent sulfur for periods of 1, 3, and 5 days at 4.2, 12.7, and 21.1 kg. per sq. cm. oxygen pressure, respectively. In general, they found that the aging rate did not increase in proportion to the pressure. The present authors were also unable to find data on the effect of increasing the

temperature of the test beyond 70° C. The present investigation was undertaken to obtain additional information on the pressure-temperature relation in the test and to lay the foundation, if possible, for improvements in the procedure as it is now conducted. It was hoped that some new conditions could be adopted which would accelerate the test since, with the development of superaging compounds, aging periods of 10 days or more are sometimes required for their evaluation. Such long periods of test require more equipment and add to the delay and expense of laboratory work. Also, if lower oxygen pressures could be used, the occasional misgivings that have been voiced as to the safety of the apparatus might be removed.

### Compounds and Procedure

The compounds shown on the next page were chosen for this investigation.

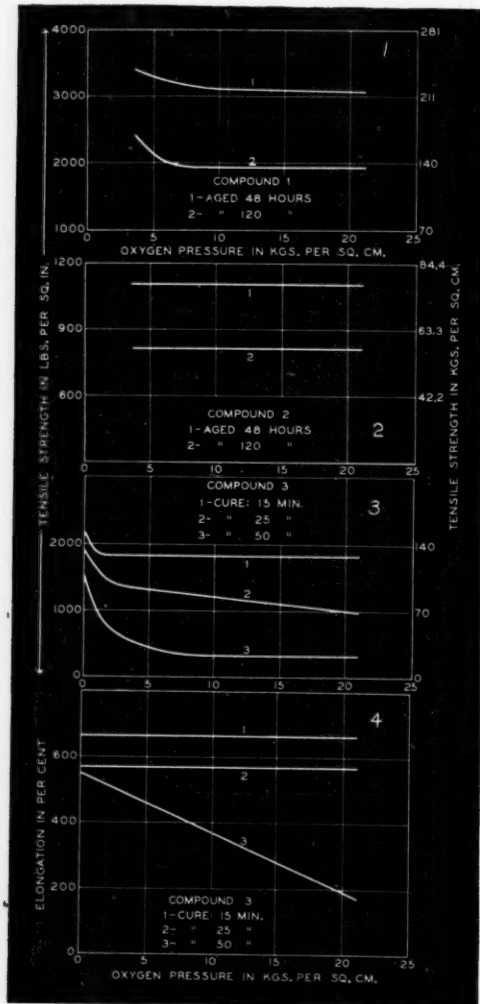
The procedure followed in the preparation of compounds and molded sheets was that recommended by the Physical Testing Committee of the Division of Rubber Chemistry, AMERICAN CHEMICAL SOCIETY (1). Compound 1 was cured for 40 minutes at 142° C., and compound 2, 16 minutes at 135° C.; the best cure in each case was determined by tensile strength tests. Compound 3 was used by Bierer and Davis in their original investigation (2). Data were obtained on three cures which were 15, 25, and 50 minutes at 142° C. Five tensile specimens, together with blank strips of the vulcanized compound to make a charge equal to about 0.4 gram of compound per 16.4 cc. of bomb volume, were aged under each set of conditions. The average tensile strength and elongation were determined in accordance with A. S. T. M. standard procedure for evaluating aging effects.

Material	Compound		
	1	2	3
Pale crepe	100.00	...	...
Smoked sheets	....	25.00	100.00
Reclaimed rubber	....	10.00	....
Mineral rubber	....	10.00	....
Zinc oxide	20.00	1.25	....
Lithopone	....	10.00	....
Whiting	....	41.10	50.00
Sulfur	3.0	1.25	6.00
Litharge	....	0.25	10.00
Tetramethylthiourea monosulfide	....	0.15	....
Di- <i>o</i> -tolylguanidine	0.75	....	....
Phenyl- $\alpha$ -naphthylamine	0.15	1.00	....

### Effect of Pressure

Compounds 1 and 2 were aged at 70° C. under oxygen pressures of 3.5, 7.0, 14.0, and 21.1 kg. per sq. cm. for 48-hour and 120-hour periods. Compound 3 was aged in oxygen for 16 hours at 70° C. at atmospheric and at 1.75 kg. per sq. cm. pressure as well as at the pressures given above. The tensile properties of these compounds before and after aging were determined and are given in Tables I, II, and III, and plotted in Figures 1, 2, and 3. For compound 1 the results appear to

indicate conclusively that the rate of aging does not increase with increased oxygen pressure between 7.0 and 21.1 kg. per sq. cm. In the case of compound 2 no change in aging rate occurs between 3.5 and 21.1 kg. per sq. cm. For compound



FIGURES 1 TO 4. EFFECT OF OXYGEN PRESSURE ON AGING

3, cured 15 minutes, no variation in aging rate is shown for oxygen pressures between 1.75 and 21.1 kg. per sq. cm., but somewhat less deterioration occurs in aging at atmospheric pressure. In the case of the 25- and 50-minute cures, much

TABLE I. TENSILE STRENGTH AND ELONGATION OF COMPOUND 1 BEFORE AND AFTER AGING AT 70° C. AND VARIOUS OXYGEN PRESSURES

	Tensile Strength		Decrease %	Elongation %
	Lb./sq. in.	Kg./sq. cm.		
Unaged	3675	257.3	..	745
Aged 48 hours at:				
3.5 kg./sq. cm.	3375	236.2	8.1	770
7.0 kg./sq. cm.	3180	222.6	12.4	740
14.0 kg./sq. cm.	3250	227.5	11.5	750
21.1 kg./sq. cm.	2860	200.2	22.1	760
Aged 120 hours at:				
3.5 kg./sq. cm.	2395	167.6	34.8	745
7.0 kg./sq. cm.	1900	133.0	48.3	740
14.0 kg./sq. cm.	2000	140.0	45.5	710
21.1 kg./sq. cm.	2040	142.8	44.4	740

TABLE II. TENSILE STRENGTH AND ELONGATION OF COMPOUND 2 BEFORE AND AFTER AGING AT 70° C. AND VARIOUS OXYGEN PRESSURES

	Tensile Strength		Decrease %	Elongation %
	Lb./sq. in.	Kg./sq. cm.		
Unaged	1285	89.9	..	495
Aged 48 hours at:				
3.5 kg./sq. cm.	1110	77.7	13.6	425
7.0 kg./sq. cm.	1110	77.7	13.6	435
14.0 kg./sq. cm.	1080	75.6	15.9	430
21.0 kg./sq. cm.	1110	77.7	13.6	425
Aged 120 hours at:				
3.5 kg./sq. cm.	825	57.7	35.8	460
7.0 kg./sq. cm.	870	60.9	32.4	465
14.0 kg./sq. cm.	800	56.0	37.7	450
21.0 kg./sq. cm.	755	52.8	41.3	470

TABLE III. EFFECT OF ACCELERATED AGING AT 70° C. FOR 16 HOURS AT VARIOUS OXYGEN PRESSURES ON THE TENSILE STRENGTH AND ELONGATION OF COMPOUND 3

	Tensile Strength		Decrease	Elongation
	Lb./sq. in.	Kg./sq. cm.	%	%
15-Minute Cure				
Unaged	2806	196.4	..	655
Aged at:				
Atm. pressure	2162	151.3	23.0	652
1.75 kg./sq. cm.	1795	125.6	36.0	648
3.50 kg./sq. cm.	1796	125.7	36.0	690
7.00 kg./sq. cm.	1815	127.0	35.4	690
14.00 kg./sq. cm.	1864	130.5	33.5	688
21.10 kg./sq. cm.	1818	127.3	35.3	666
25-Minute Cure				
Unaged	2821	197.5	..	641
Aged at:				
Atm. pressure	1897	132.8	32.6	575
1.75 kg./sq. cm.	1463	102.4	38.2	602
3.50 kg./sq. cm.	1324	92.7	53.0	588
7.00 kg./sq. cm.	1216	85.1	56.7	608
14.00 kg./sq. cm.	1024	71.7	64.0	576
21.10 kg./sq. cm.	971	68.0	66.0	535
50-Minute Cure				
Unaged	2334	163.4	..	661
Aged at:				
Atm. pressure	1508	105.6	35.5	550
1.75 kg./sq. cm.	733	51.3	69.0	435
3.50 kg./sq. cm.	558	39.0	76.0	430
7.00 kg./sq. cm.	313	22.0	87.0	366
14.00 kg./sq. cm.	259	18.1	89.0	296
21.10 kg./sq. cm.	337	23.6	86.0	168

greater increase in aging rate occurs with increased pressure than in the case of the samples cured for 15 minutes. Variation in oxygen pressure has no effect on the deterioration of elongation in the case of the 15- and 25-minute cures, but in the case of the 50-minute cure increased oxygen pressure causes a decided increase in deterioration as is shown in Figure 4.

TABLE IV. EFFECT OF VARIATIONS IN TEMPERATURE, OXYGEN PRESSURE, AND TIME ON ACCELERATED AGING OF COMPOUND 1

	Tensile Strength			Elongation
	Lb./sq. in.	Kg./sq. cm.	De-crease %	
Unaged	4055	283.8	..	745
Aged 24 hr. at 3.5 kg./sq. cm. and				
75° C.	3720	260.4	8.3	750
80° C.	3600	252.0	11.2	770
85° C.	1770	123.9	56.3	700
Aged 24 hr. at 7.0 kg./sq. cm. and				
75° C.	3478	243.5	14.2	734
80° C.	2654	185.8	34.6	735
85° C.	1469	102.8	63.8	665
Aged 48 hr. at 3.5 kg./sq. cm. and				
70° C.	3375	236.2	8.1	770
75° C.	2263	158.4	44.2	707
80° C.	1682	117.7	58.6	680
85° C.	1440	100.8	64.5	670
Aged 48 hr. at 7.0 kg./sq. cm. and				
70° C.	3180	222.6	12.4	740
75° C.	2128	149.0	47.6	690
80° C.	899	62.9	77.9	625
85° C.	355	24.8	91.2	550

TABLE V. EFFECT OF VARIATIONS IN TEMPERATURE, OXYGEN PRESSURE, AND TIME ON ACCELERATED AGING OF COMPOUND 2

	Tensile Strength			Elongation
	Lb./sq. in.	Kg./sq. cm.	De-crease %	
Unaged	1048	73.4	..	515
Aged 24 hr. at 3.5 kg./sq. cm. and				
75° C.	913	63.9	12.9	480
80° C.	890	62.3	15.1	480
85° C.	790	55.3	24.6	460
Aged 24 hr. at 7.0 kg./sq. cm. and				
75° C.	988	69.2	5.7	475
80° C.	873	61.1	16.7	462
85° C.	746	52.2	28.8	454
Aged 48 hr. at 3.5 kg./sq. cm. and				
75° C.	840	58.8	19.8	470
80° C.	770	53.9	26.5	460
85° C.	703	49.2	33.0	445
Aged 48 hr. at 7.0 kg./sq. cm. and				
75° C.	820	57.4	21.8	445
80° C.	725	50.8	30.8	445
85° C.	654	45.8	37.6	430

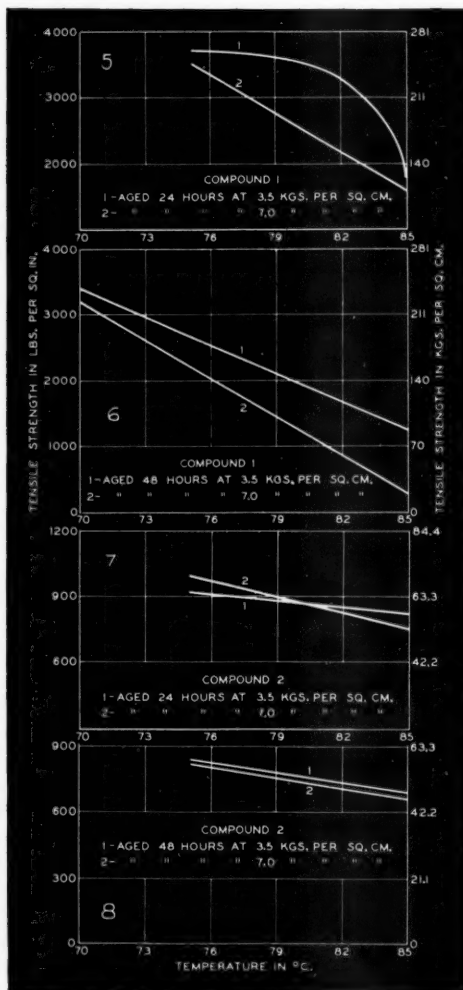
### Effect of Temperature

Compounds 1 and 2 were aged under 3.5 and 7 kg. per sq. cm. oxygen pressure for 24 hours at 75°, 80°, and 85° C., and for 48 hours at 70°, 75°, 80°, and 85°. The tensile properties of these compounds before and after aging are given in Tables IV and V and plotted in Figures 5 to 8. For the most part the data show comparatively small differences in the extent of



aging which occurs at the two pressures employed. This is particularly true in the case of compound 2.

With increased temperature, the rate of aging increased markedly. This increase was not so rapid with compound 2



FIGURES 5 TO 8. EFFECT OF TEMPERATURE ON AGING

as with compound 1. With compound 2 the percentage deterioration was approximately doubled with the 10° C. rise in aging temperature. In the case of compound 1, however, the temperature coefficient was much higher and varied widely.

### Effect of Other Variables

In the accelerated aging of rubber there are several variables besides temperature and pressure which may influence the results obtained. It is well known that appreciable variations are introduced in the tensile testing procedures and in the variations of mixing and curing the rubber specimens which cannot be entirely avoided by employing the best technic available.

The effect of the amount of rubber in the bomb was studied. Tensile specimens of compound 1, whose total weight varied from 0.25 to 3.00 grams per 16.3 cc. (cubic inch) of bomb volume, were aged for 48 hours at 21.1 kg. per sq. cm. and 70° C. The results are shown in Table VI and Figure 9; the conclusion drawn is that, within the above limits, variation in bomb loading produces no significant variation in the results.

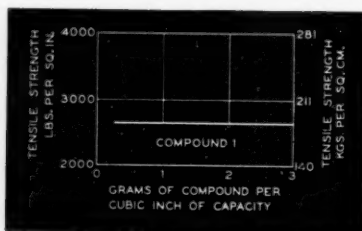


FIGURE 9. EFFECT OF BOMB LOADING ON AGING

It is well known that the oxidation of hydrocarbons results in the production of volatile products. Moisture, carbon dioxide, sulfuric acid, formic acid, and levulinic acid have been detected in the vapors given off from rubber as a result of oxidation. It was considered important therefore to determine whether the removal of these volatile substances during the aging period would influence the results. It was found that periodic flushing of the bomb (every 24 hours) as compared with nonflushing for a 120-hour aging period caused no greater variation than normally occurs in tensile testing. Data obtained on compound 1 are shown in Table VII. In recent activities with the A. S. T. M. Aging Committee, several laboratories carried out similar tests and also concluded that periodic flushing of the apparatus during testing is not necessary. This point was important since it frequently happens that the bomb is opened at intervals to remove samples during test runs over various periods.

In many cases it has been found that different rubber compounds can be placed together in the pressure vessel without affecting the aging results. However, when comparing certain antioxidants with one another and with blanks, it has been found desirable to keep them separate. Difficulty in this connection was first encountered with the evaluation of

antioxidants as compared with blank samples containing no antioxidant. The results of one of these tests showed that the tensile strength of specimens containing an antioxidant decreased 27 per cent and the blank 53. In another test, specimens of the same compound containing a more volatile antioxidant show the same 27 per cent decrease in tensile strength whereas the tensile strength of the blank decreased only 39 per cent. It is known that many antioxidants have an appreciable vapor pressure at 70° C., and the protective effect on the blank specimen is attributed to the presence of the antioxidants in near-by specimens. To avoid the effect of one compound on another, some laboratories place the test pieces of each stock in individual cans with a few small holes in the cover to admit oxygen.

### Air Bomb Test

Because of the need for testing inner tubes under conditions simulating severe service, the air bomb test has come into use. This test is being operated under somewhat different conditions in various laboratories, but common conditions are 127° C. and 5 kg. per sq. cm. air pressure. It is far more severe in effect than the Bierer-Davis oxygen test and undoubt-

TABLE VI. EFFECT OF BOMB LOADING

Bomb Content		Tensile Strength		Elongation
Compound per 16.4 cc. vol.	Rubber per 16.4 cc. vol.	—		
Grams	Grams	Lb./sq. in.	Kg./sq. cm.	%
0.25	0.20	2675	187.2	670
0.50	0.40	2575	180.3	675
1.00	0.807	2625	183.8	690
2.00	1.61	2540	177.8	710
3.00	2.42	2650	185.5	710
Unaged	...	3850	269.5	700

TABLE VII. EFFECT OF FLUSHING THE BOMB ON THE AGING OF COMPOUND I

Sample	Tensile Strength					
	Aged 120 Hr. at 70° C. and 21.1 Kg./Sq. Cm. (300 Lb./Sq. In.) Oxygen					
	Bomb Flushed Every 24 Hr.		Bomb Not Flushed			
	Unaged					
	Lb./sq. in.	Kg./sq. cm.	Lb./sq. in.	Kg./sq. cm.	Lb./sq. in.	Kg./sq. cm.
1	3500	245.0	1900	133.0	2050	143.5
2	3275	229.3	2050	143.5	1950	136.5
3	3750	262.5	1850	129.5	2150	150.5
4	3800	252.0	2000	140.0	2050	143.5
5	3500	245.0	2300	161.0	2000	140.0
Av.	...	...	2020	141.4	2040	142.8

edly simulates the particular service conditions to which inner tubes of truck and bus tires are subjected more closely than does the Bierer-Davis test.

Although the air bomb test was developed for a special purpose, there has been a recent tendency to adopt it in place of the oxygen bomb as a general aging test. Before this is done, some further work should be carried out on a variety of rubber compounds correlating the results with storage and service

aging tests. This test would probably emphasize greatly the aftervulcanization effect, particularly in stocks containing appreciable amounts of free sulfur and active accelerator. On account of the high temperature used in the air bomb test, the rate of oxidation of the rubber would be very rapid. This condition should be considered in connection with the hazard problem.

### **Suggested Modifications of Oxygen Pressure Test**

A consideration of the result of the pressure aging work here reported would appear to justify reducing the oxygen pressure to 50 pounds per square inch (3.5 kg. per sq. cm.) and raising the temperature to 80° or 85° C. The present authors consider the test at 50 pounds per square inch and 80° C. to be as safe as, if not safer than, the present test where such a large surplus of oxygen is present. The principal object of using the new conditions is to accelerate the test. When this is accomplished, a less cumbersome apparatus can undoubtedly be designed for the purpose, and, with the elimination of most of the high-pressure hazard, the test need not be surrounded with all of the safety routine now required. Calling the apparatus an "oxygen pressure" aging test rather than a "bomb" test would also go far towards eliminating present odium now surrounding the method and make it easier to satisfy building engineers that the apparatus need not be isolated and surrounded with safety walls, etc.

Considerable time is used in opening and closing the present apparatus, which involves the use of a bolted cover. With lower oxygen pressures a quick-acting closure could be employed. The open water bath is an objectionable feature in the present apparatus, and it is proposed to use small jacketed autoclaves with circulating water in the jacket. These autoclaves need not be built of such heavy material to stand the lower pressure, and they can be equipped with safety blow-out devices to take care of any rapid combustion that might occur within the autoclave.

For laboratory work it is preferred to have a series of small autoclaves rather than large ones. The apparatus will thus be far more flexible, making it possible to separate the different compositions to a greater extent and should result in considerable time saving for the operator. Work is proceeding in connection with the design of such equipment, which should represent a distinct improvement over that now available. In those cases of routine inspection, however, where a considerable number of samples representing a single lot of material are to be tested, the present larger apparatus with some alterations may be preferable to several small units.

Before any new set of conditions for the oxygen pressure aging test is finally adopted, it will be desirable to accumulate additional data on a wider range of rubber compositions than were involved in this investigation.

### Acknowledgment

Acknowledgment is made to G. N. Vacca, who was responsible for carrying out much of the experimental work involved in this paper.

### Literature Cited

- (1) Am. Chem. Soc., Div. of Rubber Chem., Physical Testing Comm., *Rubber Age* (N. Y.), Jan. 25, 1930.
- (2) Bierer and Davis, *Ind. Eng. Chem.*, **16**, 711-17 (1924).
- (3) *Ibid.*, **17**, 860-8 (1925).
- (4) Williams and Neal, *Ibid.*, **22**, 874 (1930).

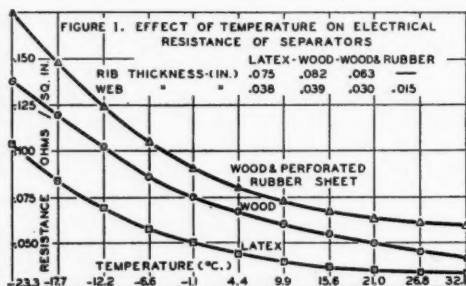
# Latex Battery Separators

## Preparation and Properties

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THE commonly used electrical storage battery consists of alternate negative plates of sponge lead and positive plates of lead peroxide immersed in an electrolyte, sulfuric acid; the whole is enclosed in a hard rubber or bituminous composition case. These plates are ordinarily separated from one another by ribbed sheets of wood called "separators." The separators prevent short circuiting of the plates caused by actual contact of the plates with each other or by "treeing" (formation of lead crystals between the plates). The separators must be thin, in order to make the battery as compact as possible, and yet must be durable. It is necessary that they be highly porous so that their electrical resistance will be low, but the pores must be sufficiently fine so that "treeing" does not take place.



Wood separators are ordinarily made of Port Orford cedar. They are usually given a preliminary treatment in warm, dilute sodium hydroxide solution to swell them, thus increasing their porosity, and to remove injurious substances which cause self-discharge and corrosion of the plates. Wood separators have the advantage of being inexpensive and of having fairly low electrical resistance, but they are not so resistant to the action of sulfuric acid and the oxidizing action in the cell as is desirable. They are, in many cases, the first part of the storage battery to fail and must then be replaced if the battery is to give further service.

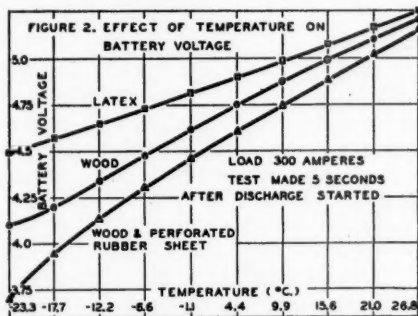
Many materials have been used as substitutes for wood in battery separators. Among them are finely divided, fritted glass (12), thin sheets of wood coated with rubber (6), asbestos and zinc dust molded with a phenolic condensation product



and treated with acid to remove the zinc (5), sliced tripoli (2), cloth or paper impregnated with synthetic gum (16), Filtros treated with hydrous silica (14), aluminum oxide with a vitrified bonding material (1), cloth coated with celluloid (4), bird feathers treated with sodium sulfite (19), cork or wood bound with latex (10), pyroxylin and sodium silicate mixtures (11), etc. As far as the present writers know, none of these materials have been used extensively.

Rubber, especially ebonite, has been much more successful than any other material as a substitute for wood in battery separators. In 1915 Willard (18) prepared "thread rubber" separators by plying up layers of fabric or cords coated with hard rubber stock, slicing in a direction perpendicular to the cords, and curing the slices. The use of sheets of perforated hard rubber in conjunction with wood separators has been common in the industry for several years in some types of batteries. Wilderman (17) prepared hard rubber separators with fine pores either by binding hard rubber dust with a hard rubber cement and curing the resulting product under light pressure, or by curing semi-cured hard rubber dust under light pressure without a binder.

Recently, the commercial production of porous ebonite separators from latex has been started (3, 7, 9). In 1915 Schidrowitz (13) discovered that a porous product could be obtained by vulcanizing coagulated latex under such conditions that the serum was retained in the coagulum during vulcanization. The latex coagulum has a reticulated structure; that is, both serum and rubber are continuous phases.



The same thing was observed by Hopkinson (8), who vulcanized a plastic, highly compounded latex mixture in open steam to form a product which was porous when cured. By using sufficient sulfur, a porous ebonite product may be obtained by the Schidrowitz process. It is a product of this type that is used for battery separators.

### Preparation of Latex Separators

For the purpose of comparing latex and wood separators, the former were prepared from a mixture of the following composition (in grams):

Centrifuged latex (60% rubber)	166.6
50% sulfur suspension	96
40% zinc oxide suspension	5
Ethylene diamine	5
Mercaptobenzothiazole	1.6
25% diphenylguanidine suspension	7.1
Water	15.3
	<hr/> 296.6

The sulfur and diphenylguanidine suspensions, which contained glue as the protective colloid, were ground in a pebble mill. The zinc oxide suspension, which contained Saprotin (a commercial dispersing agent), was also ground in the pebble mill. This mixture was poured into a mold having the shape of a battery separator and cured in open steam until at least 90 per cent of the sulfur present was combined.

### Electrical Characteristics of Latex and Wood Separators

Since starting and lighting batteries are required to furnish discharge currents of as high as 300 to 500 amperes, low internal resistance, and therefore low resistance of the separators, is of great importance. In this work the resistances of latex separators, Port Orford cedar separators (soaked in acid for 3 weeks), and a combination of Port Orford cedar and perforated hard rubber sheets were determined. The sheets were 0.015 inch (0.38 mm.) thick and contained small diamond-shaped perforations which gave them a porosity of approximately 48 per cent. The method described by Vinal (15) was used in making the measurements. A hard rubber battery case, containing two diaphragms approximately 2 mm. apart, was filled with sulfuric acid of 1.280 specific gravity (26.6° C.). The diaphragms contained circular holes over an area of 10 square inches (64.5 sq. cm.). Current and potential electrodes were placed on each side of the double diaphragm, and the potential difference set up by the current electrodes was measured by means of a Kelvin bridge equipped with an alternating current galvanometer. The separator was placed between the two diaphragms, and its effect upon the potential difference measured. Figure 1 shows the results obtained at 80° F. (26.7° C.), 40° F. (4.4° C.), 10° F. (-12.2° C.), 0° F. (-17.8° C.), and -10° F. (-23.3° C.). The difference in electrical resistance between latex and wood, or wood and perforated rubber sheets, increases as the temperature becomes lower.

The effect of this difference in electrical resistance upon the performance of a battery, as measured by terminal voltage, is shown in Figure 2. Three-cell, thirteen-plate batteries, containing positive plates  $5\frac{3}{8}$  inches (13.65 cm.) high,  $5\frac{1}{8}$  inches (14.29 cm.) wide, and 0.100 inch (2.54 mm.) thick, and negative plates  $5\frac{3}{8}$  inches high,  $5\frac{1}{8}$  inches wide, and 0.90 inch (2.29 mm.) thick, were insulated with the three types of separators. The batteries were placed under a load of 300 amperes, and their terminal voltages were measured 5 seconds after the start of the discharge. The batteries were

cooled in a mechanical refrigerator for the tests made at temperatures below 80° F. (26.7° C.). The lower electrical resistance of the latex separators, especially at low temperatures, is demonstrated by the higher voltage of the battery containing them.

To determine just how much this higher voltage of the battery containing latex separators would mean in actual service,

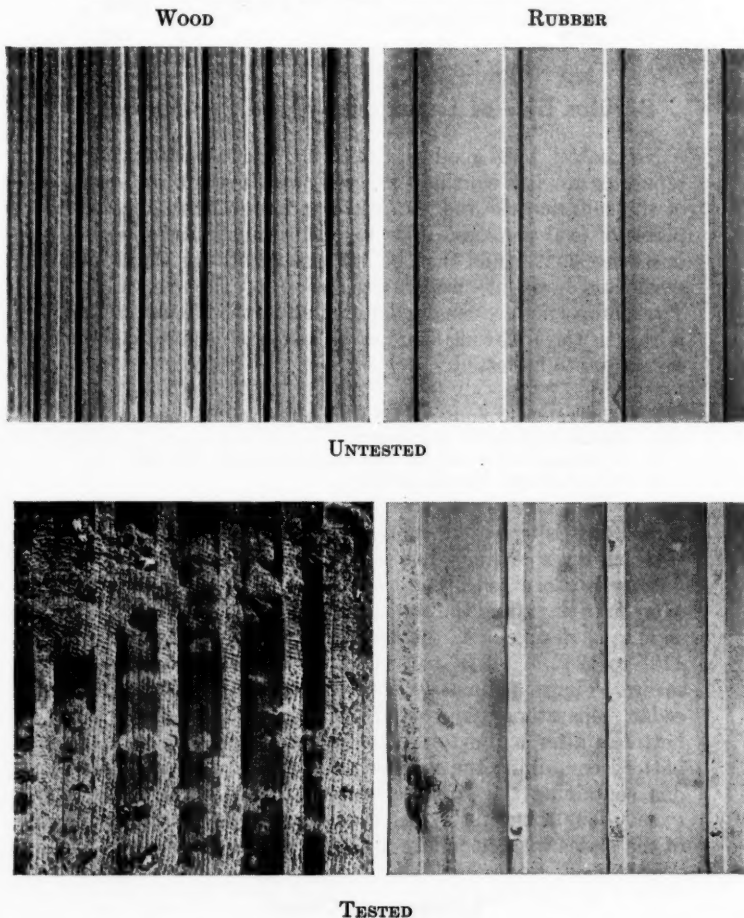


FIGURE 3. COMPARISON OF CEDAR AND LATEX SEPARATORS BEFORE AND AFTER A LIFE TEST OF THIRTEEN THOUSAND CYCLES IN A BATTERY

the speed at which batteries containing the three types of insulation would turn an automotive starting motor, under constant load, was determined. A Prony brake was connected to a starting motor taken from one of the popular lightweight cars. The tests were conducted on batteries cooled to 0° F. since starter speed becomes important at low tem-

peratures. In making the tests, the brake tension on the starting motor was adjusted to cause a load of 300 amperes on the battery. The results obtained are as follows:

Separator	Battery Voltage	R. P. M. of Starting Motor
Latex	4.57	380
Port Orford cedar	4.20	278
Port Orford cedar plus perforated hard rubber sheets	3.95	220

### Service Life of Latex and Wood Separators

No matter how good the electrical characteristics of a separator are, it is worthless if it will not withstand the action of the sulfuric acid and the oxidizing action of the positive plates of lead peroxide. The separator must neither soften in service, as it would then be cut through by the plates, nor swell and prevent proper circulation of the electrolyte. These properties are usually determined by the life test, which is run in the following manner on batteries containing the separators to be tested:

1. Charge at 10 amperes for 6 minutes and 25 seconds.
2. Allow to rest for 3 minutes.
3. Discharge at a rate of 300 amperes for 5 seconds.
4. Allow to rest for 30 seconds.

This cycle is repeated continuously for 6 days. On the seventh day a capacity test is made on the battery and the battery is recharged. The cycle is again repeated continuously for 6 days, and the test is continued in the same manner as long as desired. As the battery attains a temperature of 110° to 120° F. (43.3° to 48.9° C.), the test becomes quite severe. Figure 3 shows sections of latex and of Port Orford cedar separators removed from standard thirteen-plate batteries after a life test of twelve thousand cycles. The battery containing the wood separators had failed, but the one containing the latex separator had not. Life tests of twenty-four thousand cycles have resulted in disintegration of the plates without failure of the latex separators.

### Literature Cited

- (1) Anderson, U. S. Patent 1,458,377 (1923).
- (2) Baird, *Ibid.*, 1,279,074 (1918).
- (3) Beckmann, *Ibid.*, 1,745,657 (1930).
- (4) Benner and Heise, *Ibid.*, 1,484,928 (1924).
- (5) Bliss, *Ibid.*, 1,206,983 (1917).
- (6) Carpenter, *Ibid.*, 1,087,637 (1914).
- (7) Greenup, *Ibid.*, 1,959,160 (1934).
- (8) Hopkinson, British Patent 220,591 (1922).
- (9) Madge, *Ibid.*, 377,751 (1932).
- (10) Norris, U. S. Patent 1,567,747 (1926).
- (11) Pederson, *Ibid.*, 1,732,140 (1930).

- (12) Rodman, *Ibid.*, 1,051,677 (1913).
- (13) Schidrowitz, British Patent 1,111 (1915).
- (14) Thatcher, U. S. Patent 1,393,467 (1922).
- (15) Vinal, "Storage Batteries," p. 51, New York, John Wiley & Sons, 1930.
- (16) Wales, U. S. Patent 1,366,223 (1921).
- (17) Wilderman, *Ibid.*, 1,651,567 (1927).
- (18) Willard, *Ibid.*, 1,243,368 (1915).
- (19) Wood, *Ibid.*, 1,502,455 (1924).

# Kaysam

## A Casting Process for the Manufacture of Rubber Products from Latex

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Various practicable methods of applying the solids of latex and latex mixtures in the manufacture of various types of products have been employed in this country during the past years. While meritorious within their respective fields, these processes, except that for the production of sponge rubber, all have the common limitation of being applicable only to comparatively thin articles of relatively uniform thickness. The recent introduction into this country of an important English invention, Kaysam, supplies the positive three-dimensional shrinkage control and accelerated drying method, which now opens new fields to all types of products with superior strength, stretch, tear-resistance, aging, and advantages characteristic of articles made directly of latex.

### The Kaysam Development

Confronted with the conflicting problems of distressing competition and the necessarily wasteful and uneconomic methods of producing crepe rubber soles, Walter Kay, of Sam Kay & Co., Bury, England, despaired of meeting the problem except by some workable substitution of latex for crepe rubber. The result of his experimental effort was a workable process of casting liquid latex into rubber articles without limitation of size or shape. This process became known as "Kaysam," a contracted inversion of his company's name.

This process has been applied in England during the past several years, and in various continental European countries to the volume production of many types of soles, metal-inserted heels, cloth-inserted boots, and various kinds of molded articles, including those of solid and hollow construction. More recently still, Kaysam, supplemented by other important inventions of prominent American technologists relating to the fundamentals of latex compounding and use, has been made available to manufacturers in this country by the Kaysam Corporation of America.

### The Kaysam Process

Briefly expressed the Kaysam process is a method of casting hollow, semi-hollow, or solid rubber articles of any shape or size from liquid latex, compounded or not, in non-porous metallic forms, by employing a short sequence of simple operations varying somewhat with the specific product. It consists essentially of the following steps:

1. Sensitizing a liquid latex mix to cause solidification to an irreversible gel when desired.
2. Pouring the sensitized latex into a suitably designed aluminum mold.
3. Solidifying the mold-encased liquid by permitting it to stand at room temperature or by the application of heat, such as submersion into hot water.
4. Removing the gelled casting from its mold and washing in warm water to inhibit shrinkage and to improve the quality of the resultant product.



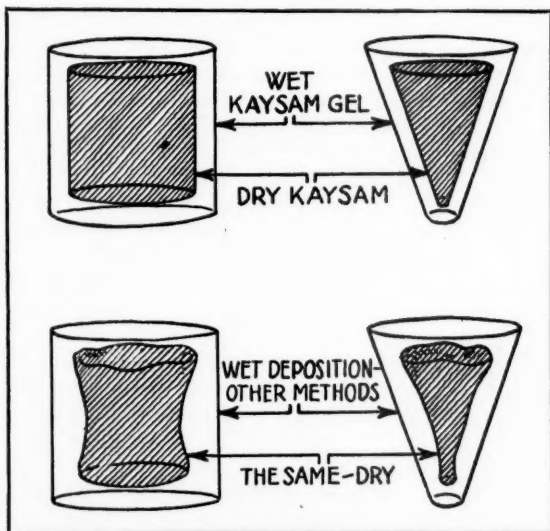
5. Drying by accelerating the natural water expelling property inherent in a gell of this structural type.

6. Vulcanizing in steam, hot water, or hot air.

#### Kaysam Sensitizing

The Kaysam process applies with equal efficacy to preserved natural or artificial latex dispersions of practically all types, compounded or not, but in either event preferably of 60 to 70 per cent concentration, containing zinc oxide or zinc salts.

According to the preferred procedure, suitable quantities of these salt solutions are added to the prepared mix to make it sensitive to temperatures slightly above room temperature and as high as 90° C. This reactive temperature can be defi-



**Kaysam Products Shrink as They Dry from the Interior, but Retain Their Shapes. By Other Methods Bulky Articles Distort as They Dry from the Exterior; Thus Kaysam Mold Sizes Can Be Calculated by Precise but Simple Mathematical Formulas**

nitely controlled, and the resulting mix is indefinitely stable below the desired critical temperature. Upon the application of heat the stability of the compound, which normally has been sufficient to protect the individual particles from coalescence while in Brownian movement, is decreased, resulting in a simultaneous and uniform coherence of the individual particles to a tough, irreversible gel.

Careful consideration of the available facts indicates that the essential difference in the method of formation of Kaysam gel and a coagulum is the uniformity of coherence throughout the mass of latex particles. Stated another way, the gel is formed by the coherence of a large number of very small particles, so that the resulting gell possesses very small voids, whereas coagulum is formed by the coherence of a few relatively large aggregates (built up, to be sure, from very small initial particles) having a structure possessing large voids, which is mechanically weak and holds the entrapped water very loosely. It is the uniform formation of the solid and liquid phase of the mix into two continuous phases which constitutes

this gel structure, with uniform shrinkage and syneresis that accelerates drying of the mass to a non-porous dry solid.

This gel structure is immersed in water to enhance syneresis, and also to prevent the formation of an air dried surface film. This step in the process also improves the quality of the product by leaching out soluble substances. Because of the nature of this gel, shrinkage, unless restricted, takes place to the same degree in all dimensions, a vital point that distinguishes Kaysam from all other methods.

### Kaysam Casting

The casting of rubber articles by the Kaysam process is performed by merely pouring the liquid composition into the desired mold or former. If stationary, it gels into a shape outwardly conformable to and identical with the cavity of the container. A semi-hollow object can be formed by gelation of the mix in a mold provided with an insert or core. Variations in thickness of any section of a molded object have no effect on gelation in the mold; the thickness is entirely controlled by the space between the mold and the core. If the mold comprises two or more parts assembled to form a complete enclosure around the mix, the gel can be formed into a hollow seamless article, *e. g.*, a hollow ball. This is accomplished by rotating the mold so as to permit the liquid to come into contact with every part of the interior. The wall thickness of a hollow article is controlled by the amount and concentration of the mix used and by the gyrations of the mold during gelation.

The following are typical examples of Kaysam castings.

**Boots.**—For casting a boot, the mold is tooled inside to the exterior contour of a finished boot, including the design or engraving of the sole, heel, etc. A core of the final shape of the inside of the boot is set into the outer mold. These two main mold parts are aligned by means of dowels, and a suitable mix is poured to fill the space between mold and core. The mold is then allowed to stand until gelling occurs at room temperature, or preferably is heated by immersion in water to shorten the operating cycle. The mold is then taken apart, and the casting is washed and allowed to dry partially. It is then drawn on to a last previously wrapped with a boot lining, and is allowed to shrink on to and assume the shape of the last. Bonding between the rubber and the lining is brought about by the inter-application of a suitable adhesive.

**Soles.**—Casting shoe soles and heels in an open mold is similar to that of a boot, except that no cloth insert is used in the former, but metal washers are fitted to the mold in the latter. A large number of sizes and thicknesses of the product can be made from one size of mold by varying the amount or the concentration of the mix, or by both means together.

**Hollow Articles.**—In the preparation of hollow articles such as toys or balls, the mold is disassembled, and the requisite amount of mix properly sensitized is poured in, the mold closed, set into a rotating machine, and revolved about two or more axes in a steam bath or through hot water. The article builds up on the inside of the mold by the progressive deposition of the gel to form a uniform or controlled wall thickness. In the case of toy animals or hollow play balls, the articles are washed, dried, and vulcanized. In some cases, however, especially with balls, it is possible to produce an article much greater in diameter than its original cast size. This is accomplished by inflating the ball shortly after its removal from the mold, thus forming a hollow casting made in a six-inch mold, for example, into balls ranging from the mold size through those of a rugby or basketball bladder to that of beach balls or larger. As the ball is inflated, its wall thickness decreases, but there is a gain in its unit strength.

### Material Economy

By the Kaysam procedure an absolute reproduction of the finest and most detailed mold surface markings or engravings may be obtained. The engraver's art loses nothing of fineness in reproduction, since shrinkage takes place during the drying of the gel. This results in detail even finer than that in the mold.

If gelling is accelerated by the application of heat, and the operating cycle thus shortened, pre-heating of sections where the gel is to be thicker is sometimes resorted to, but neither this step nor the one of actual heating are prerequisites to the formation of a proper gel.

Regardless of the type of product, waste is cut to negligible proportions, overflow is practically non-existent, the problem of using up vulcanized scrap is eliminated for most articles, scorching is avoided, material transportation and handling problems are boiled down to a matter of piping and pumping, and batching can be done—and is preferably done—in relatively large units.

### Shrinkage

As previously stated, the uniform three-dimensional shrinkage made possible by the particular gel structure and drying principles of Kaysam furnishes the missing link that opens the way to produce every known type of rubber article directly from latex. In addition, other articles will now give way to latex which either could not be made at all of masticated rubber methods or could be done only with great difficulty and exorbitant expense.

Mold design is simplified, since press pressure is not required, and since undercuts may exist without presenting difficulties in the unloading operation.

The drying of this gel gives a final product which is an exact replica of the wet one except for size. Proportionately it is identical, because drying of this reticulated structure proceeds from the interior. The distortion of thick and irregular articles attempted by porous mold or form deposition methods is due to agglomeration of the particles and to drying at the surface first. This is illustrated diagrammatically by the accompanying drawings of cylindrical and conical shaped articles, each of Kaysam and absorption methods.

There is thus a definite mathematical relation between the original and final dimensions of the Kaysam casting for any latex mix of known concentration of solids. Therefore the size and the shape of a mold can be calculated from the known dimensions of the finished article and the components of the latex mix. Conversely the article size is also calculable.

## Physical Testing Procedure for Latex Stocks

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**A**LTHOUGH procedures for the preparation of physical testing slabs from milled rubber stocks have been standardized, no such specifications are available for latex stocks. Test slabs from latex require special treatment and, if certain conditions are not fulfilled, erratic results will be obtained. The term "physical testing" as used here means the elongation modulus and tensile readings usually determined on the Scott testing machine. The procedure herein described is not set up as a complete specification, but it does give a method by which accurate and reproducible results have been obtained in this laboratory. It further calls attention to the fact that a latex stock containing more or less standard compounding ingredients (of which some are water-soluble) may be greatly altered in its physical properties by a variation in the humidity conditions under which it is being tested. All tests in this investigation were made on pure gum stocks, which experience has shown to give the most erratic results. While it is true that test strips made from factory-produced articles may give sufficient information for factory control, it is also considered essential to have available a test method for use in obtaining basic information on accelerator-sulfur ratios and general compounding ingredients.

Two methods have been proposed in the literature. One (2) recommends drying the latex test film on a glass plate placed in an oven at 45° C. The other (3) recommends drying the test films on unglazed tile, the edges of which have been built up with strips of paraffined paper to form a tray for drying the latex mix. In this investigation the glass-plate method was adopted in preference to the porous-tile method, in order to eliminate any loss of water-soluble substances originally contained in the latex or added during compounding.

In making a latex mix to be used in forming a test slab, three conditions must be considered—namely, proper viscosity of the mix, uniform fine dispersion of the pigments, and a perfectly smooth surface on the dried slab. The viscosity of the mix must be high enough to prevent settling of the pigments during drying, yet low enough to allow all air bubbles trapped during mixing to rise to the surface in a reasonable length of time before the slabs are poured. The dried surfaces of the slabs must be entirely free from ridges, cracks, or other blemishes.

All compounding ingredients used were made up in the form of water dispersions or solutions before being added to the latex. The zinc oxide and sulfur dispersions were of 40 and 50 per cent concentrations, respectively, and were prepared in a ball mill in which they were ground for 48 hours. The zinc oxide was dispersed in a 2 per cent Saprotin solution and the sulfur was dispersed in a 10 per cent glue solution. The basic test formula was of 50 per cent total solids content as follows:

	Grams
60% centrifuged latex	166
40% zinc oxide dispersion	2.5
50% sulfur	3
Piperidine pentamethylene dithiocarbamate (Pip-Pip)	0.75
10% ammoniacal casein	10
Water	26.25

The test mix was prepared by adding first the casein and then the pigments to the latex. The mix was stirred for 10 minutes at 350 r. p. m. with a single-blade mechanical stirrer and then strained through fine jersey knit rayon cloth. The strained mix was placed in a special buret and allowed to stand for 0.5 hour before the slabs were poured. During this time the air bubbles rose to the surface.

The above-mentioned burets were constructed from 71-cm. (28-inch) lengths of 29-mm. (1.125-inch) glass tubing, graduated into 25-cc. divisions and fitted at the bottom with stopper, tube, and screw clamp. The slabs were formed and dried in plate-glass trays having inside dimensions of  $175 \times 175 \times 6$  mm. ( $6.875 \times 6.875 \times 0.25$  inch). These trays were constructed by cementing, with sodium silicate solution, 13-mm. (0.5-inch) wide strips of 6-mm. (0.25-inch) plate glass about the perimeter of 187-mm. (7.375-inch) squares of the same material.

The mix was flowed into these trays by placing the buret tube close to the bottom of the tray and allowing the compounded latex to flow slowly into the cavity. The amount of the mix used was determined by the total solids content of the compound and the desired thickness of the dried slab. With the above mix 75 cc. produced a dried slab of 1.27-mm. (0.050-inch) thickness. This was the thickness of all slabs tested in this experimental work. The filled glass trays were placed upon a level surface and allowed to dry overnight at room temperature. The slabs were then removed from the trays and after 48 hours' further drying were cured by hanging individually in an oven at 100° C. If any moisture remained in the slabs after this drying period, it was removed during the air cure which followed. It was found that even with substantial amounts of water remaining in the slab before cure, there was little effect on the physical properties at the optimum cure, provided other conditions to be discussed later were fulfilled.

After the cure, test strips were cut out with a standard A. S. T. M. die 11.1 cm. (4.375 inches) long with a 2.5-cm. (1-inch) construction and tested on the Scott machine.

### Experimental

When the first slabs were prepared using the given formula, the upper surface of the dried slabs was found to be covered with a network of fine surface cracks which would invalidate any physical tests made with them. By process of elimination the zinc oxide was found to be the pigment causing the cracked

surface. However, when 1 per cent of Aquarex D, on the weight of rubber, was added as additional stabilizer, a slab was formed which when dry had a smooth and flawless surface. Examples of the two types of surfaces are shown in Figure 1.

Several tests using the procedure outlined above for the preparation of a satisfactory slab were made to determine whether reproducible results could be obtained, but it was found that large variations occurred when the test was re-

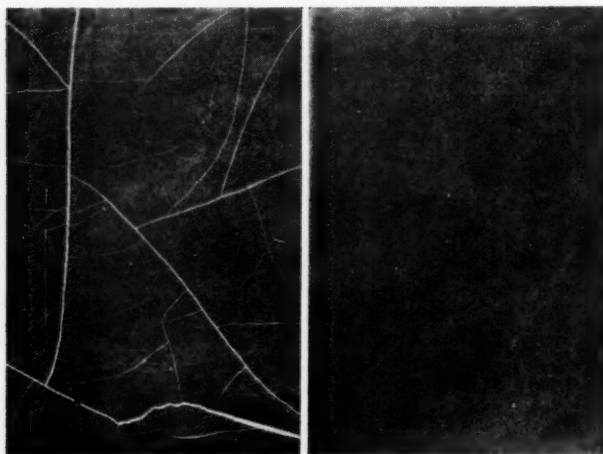


FIGURE 1. TWO TYPES OF SLAB SURFACES

peated over several days. The results of a series of this kind are shown in Table I. The slabs for this series were prepared from separate mixes on successive days using identical compounding ingredients. These slabs were also given identical drying and curing treatments. The tensile strength varied up to 25 per cent and the modulus at 600 per cent elongation varied 50 per cent.

TABLE I. RESULTS WITH TEST SLABS

Test	Elongation %	Modulus at 600 Per Cent		Tensile	
		Lb./sq. in.	Kg./sq. cm.	Lb./sq. in.	Kg./sq. cm.
1	910	500	35	4200	295
2	910	450	32	4090	288
3	870	750	53	4530	318
4	900	680	48	4570	321
5	910	620	44	4450	313
6	880	950	67	5360	377

Cures, 45 minutes at 100° C. 4 strips pulled on each test.

The well-known water-absorbing properties of latex stocks suggested that the cause of this variation might be changes in humidity which normally occur at room conditions. Therefore, tests were run in which the strips were conditioned at controlled humidities until tested. Controlled humidities were maintained in desiccators in which were placed the proper substances to give the desired moisture contents. In



the examples reported, 50 per cent relative humidity was obtained over a saturated solution of sodium dichromate, while 0 per cent humidity was obtained over calcium chloride.

The test strips, which had been cured, gaged, and bench-marked, were individually hung in a desiccator and conditioned for 48 hours, and were removed from the desiccator only as they were pulled. Table II and Figure 2 show the effect of variation in relative humidity from 0 to 50 per cent. The modulus at 800 per cent elongation and the tensile strength were both reduced approximately 30 per cent when

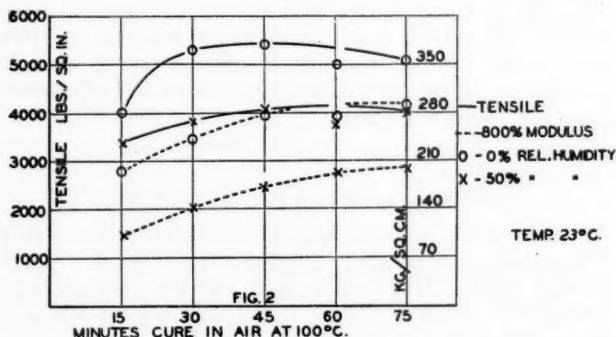


FIGURE 2. EFFECT OF HUMIDITY ON LATEX STOCK

TABLE II. EFFECT OF HUMIDITY ON LATEX STOCK

Cure at 100° C. in Air	Elongation		Modulus at 800 Per Cent				Tensile			
	0%	50%	0%	50%	0%	50%	0%	50%	0%	50%
Min.	%	%	Lb./sq. in.	Kg./sq. cm.	Lb./sq. in.	Kg./sq. cm.	Lb./sq. in.	Kg./sq. cm.	Lb./sq. in.	Kg./sq. cm.
15	900	990	2820	1440	198	101	4010	3400	282	239
30	920	930	3420	2070	240	148	5360	3870	377	272
45	900	900	3980	2490	280	175	5460	4100	384	288
60	870	850	3900	2800	274	197	4980	3850	350	271
75	850	870	4150	2880	292	202	5080	4030	357	283

3 strips tested for each cure.  
Thoroughly dried strips were conditioned for 48 hours at indicated humidity before testing.

TABLE III. CONSISTENCY COMPARISON OF LATEX STOCKS vs. MILL-MIXED PURE GUM STOCK

Test	Elongation	Modulus at 800 Per Cent		Tensile	
	%	Lb./sq. in.	Kg./sq. cm.	Lb./sq. in.	Kg./sq. cm.
Latex Stock <sup>a</sup>					
1	870	3980	280	5380	378
2	880	3680	259	5180	364
3	880	3860	271	5140	361
Mill-Mixed Stock <sup>b</sup>					
Modulus at 600 Per Cent					
1	780	940	66	3080	217
2	800	810	57	3060	215
3	800	850	60	3010	211

<sup>a</sup> Cure, 45 minutes at 100° C. 4 strips pulled on each test. 0% humidity; 23° C.

<sup>b</sup> Cure, 45 minutes at 127° C. Tested at room conditions, 23° C.

the relative humidity was increased from 0 to 50 per cent. Elongation increased slightly with increased relative humidity.

This reduction in tensile and modulus values with an increase in relative humidity showed that consistent results could be obtained only when the humidity was controlled up until the time of testing. Conover and Depew (1) recommend that regular mill-mixed stocks be conditioned at 0 per cent relative humidity before pulling. While these recommendations are not generally followed on mill-mixed stocks, it is most important that constant and preferably 0 per cent relative humidity be maintained when testing latex stocks.

In order to determine the reproducibility of results by this method (using 0 per cent humidity) the test was repeated three times, the compounding ingredients being identical in each case. A comparison was made with a mill-mixed pure gum stock of the following formula:

Smoked sheets	100
Sulfur	3
Zinc oxide	4
Mercaptobenzoethiasole	1

This stock was tested by regular methods. A comparison of the consistency of results from the two types of stocks is shown in Table III. It will be seen that the percentage deviation from batch to batch in the latex stock is favorably comparable to that of the mill-mixed variety.

### Summary and Conclusion

Adjustment of stabilizers may be necessary in order to produce a smooth surface on an air-dried latex test slab. A combination of 1 per cent of casein and 1 per cent of Aquarex D on the rubber gave a satisfactory dried slab.

Reproducible results cannot be obtained unless the test strips are conditioned at controlled relative humidity conditions. Zero per cent humidity gave highest tensile and modulus figures.

Batch-to-batch accuracy of latex stocks using methods described herein was comparable to that of mill-mixed pure gum stock.

### Literature Cited

- (1) Conover and Depew, *Proc. Am. Soc. Testing Materials*, 27, Part II (1927).
- (2) Du Pont Laboratory Report No. 181 (December 4, 1934).
- (3) *Vanderbilt News* (September-October, 1934).

# Examination of Rubber Latex and Latex Com- pounds

## Part II. Chemical Testing Methods

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**L**ATEX compounds are purchased either on the basis of total solids content or the so-called dry rubber content. The total solids probably furnish a more reliable basis of evaluation, as the determination can be made with a high degree of accuracy. The dry rubber content is not a precise determination, as the proteins, fatty acids, and other non-rubber constituents are included, and in the case of compounded latices some of the compounding materials are included in the value and some are not. Hauser (8) and Noble (9) include in their books useful chapters on testing latex.

### Total Solids

The total solids are determined by weighing about 2 grams of the sample in a low covered weighing dish about 6.25 cm. (2.5 inches) in diameter on an analytical balance. A metal weighing dish is preferred for more rapid drying. Tinned 60-ml. (2-ounce) ointment cans are satisfactory and so inexpensive that they may be thrown away if they are at all difficult to clean. The sample is dried, preferably in a vacuum oven. The temperature may be increased to 120° C. in a vacuum without any apparent oxidation or deterioration of the rubber. A sample of normal latex may be completely dried in about 10 minutes if the drying arrangement is right. Results are accurate to better than 0.1 per cent.

Methods involving the use of specific gravity are worse than useless when applied to preserved latex as a concentration control. Even in the case of unpreserved, unwatered normal latex on the plantations, the hydrometers must be calibrated especially for the latex from the estate on which they are to be used.

### Dry Rubber Content

A number of official methods for determining the dry rubber content have been described. Usually the diluted latex is coagulated with acetic acid and the coagulum dried. The various official methods usually differ only in minor details.

The method as prescribed by the Customs of the Commonwealth of Australia (4) for evaluating latex for tariff purposes is as follows:

Place a weighed quantity of latex (approximately 10 grams) in a porcelain or glass basin of about 200-ml. capacity. Add gradually, with constant stirring, a 1 per cent solution of acetic acid until the latex appears to be completely coagulated and the addition of more acid produces no apparent effect. Manipulate coagulum with stirrer until all particles are collected in one mass.

Place basin on a steam bath for 30 minutes; pour off and wash coagulum with water.

Remove coagulum from basin and pass it several times through rollers to squeeze out serum. Wash the thin rubber with water and finally dry it at 100° C. until the rubber no longer loses weight. The percentage of dry rubber so found shall be the crude rubber content of the latex tested.

The relationship between the acetic acid rubber (dry rubber content) and solids for unwatered normal latex is roughly

$$\text{Acetic acid rubber} + 2.3 = \text{total solids}$$

### Determination of Ammonia

If ammonia alone has been added to latex, it is usually satisfactory to titrate directly with standard acid, using methyl red as indicator.

Weigh about 10 grams to the nearest centigram in a 400-cc. rubber-extraction flask. Add about 200 cc. of water, a few drops of methyl red indicator, and titrate with 0.588 *N* acid, being careful to keep the solution well agitated throughout the determination. The volume of acid used divided by the weight of sample will give the percentage of ammonia. If only occasional tests are required, 0.5 *N* or 0.1 *N* acid may be used. The presence of hexamethylenetetramine does not interfere to any appreciable extent.

If other alkaline materials, such as sodium or potassium hydroxide, borax, or sodium silicate, are present in addition to the ammonia, the ammonia may be distilled over into standard acid and titrated.

Weigh about 5 grams of the sample from a weighing pipet into an 800-cc. Kjeldahl flask containing about 250 cc. of distilled water. Distill over about 200 cc. into an excess of 0.1 *N* sulfuric acid. Back-titrate the excess of standard acid with 0.1 *N* sodium hydroxide using methyl red as indicator.

$$\frac{(\text{cc. of acid} \times \text{normality factor} - \text{cc. of base} \times \text{normality factor}) \times 1.7}{\text{weight of sample}} = \% \text{ NH}_3$$

In compounds which contain no fixed alkali, the distillation method will give only the free ammonia. Ammonium soaps are also included if a little sodium hydroxide is added before the distillation. One cubic centimeter of normal caustic will take care of all the ammonium soaps which are normally present in latex.

In the presence of the alkaline materials mentioned above, total ammonia may be determined by coagulating the latex

and nesslerizing the clear serum. The method in detail is as follows:

**NESSLER REAGENT.** Dissolve 25 grams of potassium iodide in 20 cc. of distilled water. Add saturated mercuric chloride solution until a slight precipitate appears. Add 200 cc. of clear 36 per cent sodium hydroxide solution. Dilute to 500 cc., let stand one day or longer, filter through asbestos in a Gooch crucible, and place in a dark bottle. After about 24 hours the small amount of precipitate will have settled and the solution will be clear.

**STANDARD AMMONIA SOLUTION.** Dissolve 0.4176 gram of ammonium oxalate,  $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ , in distilled water and make up to 1000 cc. Pipet out 20-cc. aliquot and make up to 1000 cc. This solution contains 2 mg. of  $\text{NH}_3$  per liter.

**METHOD.** Weigh about 10 grams of the latex from a weighing pipet into a 1000-cc. volumetric flask containing about 950 cc. of water. Shake and add a dilute solution of acetic acid, a few drops at a time, shaking thoroughly between additions until the latex is coagulated. Make the volume up to the mark, mix thoroughly, and filter a portion of the serum, rejecting the first 10 to 20 cc. which do not always come through clear.

In some cases, especially with latex compounds containing pigments, antioxidants, etc., it is necessary to refilter the solution with the aid of a little Celite in order to remove opalescence. The final solution should be perfectly clear and colorless.

Measure an aliquot of this clear filtrate into a 500-cc. volumetric flask and make up to the mark with distilled water. The size of the aliquot depends on the ammonia content of the sample. A 100-cc. aliquot is used when the ammonia content is expected to be about 0.1 per cent and proportionally smaller amounts for higher percentages.

After the aliquot has been made up to 500 cc., measure 25 cc. of this diluted solution in a graduated cylinder, and treat with 1 cc. of Nessler reagent added from a pipet. Compare the color in a colorimeter with that obtained from 25 cc. of the dilute standard ammonium oxalate solution obtained in the same way. Either the distillation or nesslerization method may be applied to black or colored compounds. The color is all carried down with the rubber on coagulation.

**FIXED ALKALI.** The amount of fixed alkali present may be estimated from the difference between the total alkalinity by direct titration and the ammonia as determined either by distillation or nesslerization.

### Hexamethylenetetramine

Hexamethylenetetramine is frequently present in latex compounds. Its presence is of very little importance in most cases, as it is water-soluble and is usually removed from the finished product in the serum or by washing. It may be detected, however, by diluting the latex considerably, adding acid to coagulate and about 25 cc. of normal acid in excess, distilling off some of the water, and testing the distillate with fuchsin sulfite solution. A red or purple coloration indicates hexamethylenetetramine.

The fuchsin sulfite reagent is prepared by dissolving 0.5 gram of fuchsin and 9 grams of sodium bisulfite in 500 cc. of distilled water. Ten cubic centimeters of concentrated hydrochloric acid are added and the solution is kept well stoppered and away from light.

Hexamethylenetetramine may be determined quantitatively as follows:

Dilute the residue from the ammonia determination by distillation to about 250 cc. with water and add 25 cc. of normal acid from a buret. Boil the flask for about 5 minutes, cool, and add 26 cc. of normal caustic. Distill the ammonia into standard acid and titrate exactly as described in the ammonia by distillation method above. One cubic centimeter of normal acid is equivalent to 0.035 gram of hexamethylenetetramine.

### Determination of Water-Solubles

The amount of water-solubles in latex cannot be easily and completely leached from a latex film by merely boiling with water or extracting with water as is done in the case of the acetone extract. Using such methods, the extraction is very likely to be incomplete and the results will depend on the amount of surface of the sample extracted.

The water-solubles may be removed from the uncoagulated sample by dialyzing through a parchment membrane with distilled water, but the determination is slow, a week or more being required to remove all the extractable materials. A coagulation method which has proved very satisfactory consists of boiling off the ammonia, diluting considerably, then coagulating by adjusting to the isoelectric point of the protective proteins with a known amount of acid, evaporating an aliquot of the serum, weighing, and correcting for the acid added. The method in detail is as follows:

Weigh about 5 grams of the sample accurately to a centigram in a 400-cc. beaker, add about 200 cc. of water at once, cover with a watch glass, and boil on a hot plate until the volume has been decreased considerably.

Transfer to a 200-cc. volumetric phosphoric acid flask (this type of flask has a wide neck and is easily cleaned), and make up to within about 10 cc. of the mark, add 1 cc. of a 0.1 per cent methyl orange indicator solution, and add *N* sulfuric acid from a buret until the red-orange color, indicating a pH of about 4.3, is obtained, and the rubber is well coagulated. Care must be taken not to add too much acid, as the sample will not coagulate so well at a lower pH. Shake well to complete coagulation and make up to the mark.

Filter and pipet 100 cc. of the clear serum into a weighed evaporating dish. Evaporate to dryness on a steam bath, dry in an air oven at 70° C., cool, and weigh.

Normal latex has water-solubles of about 8.5 per cent and centrifuged or creamed latices have water-solubles of about 2.6 per cent of the total solids.

$$E = \left\{ \frac{W \left( 200 - \frac{S T R}{10,000 D} \right)}{100} (-0.0049 A + I) \right\} \frac{10,000}{S T}$$

*E* = per cent of water extract

*W* = weight of dry material in 100-cc. aliquot

*T* = per cent of total solids

*R* = percentage of rubber expected in the solids of the sample, for normal latex 92 per cent, for creamed latex 97 per cent, etc.



- $D$  = density of rubber (about 0.92)  
 $A$  = volume of 0.1  $N$  sulfuric acid used  
 $I$  = weight of indicator used, in grams  
 $S$  = weight of sample

### Acetone Extract

The acetone extract is not of very much value as a control test for consignments of raw latex, but may be of great assistance in examining samples of unknown composition, particularly compounded samples, and is a necessary part of the usual method of determining free or combined sulfur.

The film should be laid down by pouring some of the latex into a shallow glass tray, which is easily prepared from a pane of window glass and some glass rods or tubing. The glass rod is cut to fit around the edge of the plate and is stuck on with paraffin wax. The edges of the plate are then dipped in molten paraffin wax, thus making a ridge of wax supported by the rods all around the glass plate. The film should be thin and dried at room temperature until it is clear. An electric fan blown over the film hastens drying considerably. The film is then sheeted out as thin as possible on a cold roll but not broken down.

The prepared film is cut in narrow strips and 1 gram is weighed in an extraction thimble and extracted for 16 hours, according to the method and using the apparatus recommended by the committee on Methods of Analysis of the Rubber Division of the AMERICAN CHEMICAL SOCIETY for rubber goods (2). Part of the acetone may be removed by boiling on a hot plate or steam bath, but great care must be observed and the flask must not go dry. It is possible to scorch the extract on a hot plate with as much as 10 cc. of acetone remaining in the flask, and if the sample goes dry on a steam bath appreciable amounts of free sulfur may be lost. It is best to stand the flasks in a bath of warm water, 40° to 70° C., remove the acetone by gently blowing air into the flask until it is dry, and finally dry in an air oven at 70° C.

The time of extraction of 16 hours is empirical. The greater part of the extract is removed in this time, but some less easily soluble materials will not be entirely removed if the extraction is continued for several days. The thickness of the film also has some bearing on the quantity of extract removed, as has the rate of boiling.

### Free Sulfur

Free sulfur is usually determined on the acetone extract of the film. The bromine method (2) is most commonly used and is satisfactory, except that the results generally contain some if not all of the sulfur of the accelerator and may be rather confusing. The method of Bolotnikov and Gurova (5), in which the rubber film is heated with a solution of sodium sulfite, the excess of sulfite destroyed with formaldehyde, and the thiosulfate which was formed titrated with iodine,

is very convenient, but some accelerators interfere. This method was modified by Oldham, Baker, and Craytor (10) to prevent interference by mercaptobenzothiazole and is satisfactory in most cases, but tetramethylthiuram disulfide will give high results.

The method has been further modified in the author's laboratory to make it possible to run sulfur on the uncoagulated latex.

Weigh about 10 grams of the latex compound into a 400-cc. rubber-extraction flask and add 100 cc. of a 5 per cent sodium sulfite solution. Bring to the boiling point and boil gently for 5 minutes on a hot plate. Care must be taken to avoid vigorous boiling or the mixture will froth over the neck of the flask. Remove the flask from the hot plate and add 100 cc. of a 0.5 per cent strontium chloride solution and 4 cc. of glacial acetic acid. Stir until the rubber is coagulated. Remove the lump of rubber, washing it with a jet of water and squeezing it with the fingers to express as much of the liquid as possible.

To the solution add 6 cc. of 37 per cent formaldehyde, then a few drops of phenolphthalein and sufficient sodium hydroxide to turn the indicator pink. Add normal acid until the pink color completely disappears but avoid any considerable excess. Let the mixture stand about 10 minutes, then filter it, receiving the filtrate in a 1000-cc. flask. Wash the filter paper twice with a jet of hot water. Acidify the filtrate with 10 cc. of glacial acetic acid, add cracked ice to bring the temperature below 15° C. and the volume to about 600 cc., and titrate with 0.1 *N* iodine, using about 5 cc. of a 3 per cent starch solution as indicator.

1 cc. of 0.1 *N* iodine = 0.003206 gram of sulfur

Sulfur-bearing accelerators, such as mercaptobenzothiazole, xanthates, carbamates, and thiuram monosulfides, do not interfere with the determination but tetramethylthiuram disulfide is dissolved and one-fourth of its sulfur is titrated.

The above method gives the true free sulfur of the sample. The sulfur is in a fine state of division and is reacted on by the sodium sulfite almost immediately, and all chance of loss of free sulfur because of vulcanization during the determination is eliminated. When the other methods are used there is always a chance that the rubber has cured up somewhat and part of the sulfur has combined while the film was being dried or extracted.

### Total Sulfur

The Parr sulfur bomb method (11) and the nitric acid-bromine method (2) are both satisfactory. The author has, however, found the perchloric acid (12) method more convenient, rapid, and highly dependable. The perchloric acid method may be carried out as follows:

To a 1-gram sample of the latex film in a 250-cc. rubber-extraction flask add 20 cc. of a nitric acid solution 1 to 1 and warm on an electric hot plate for 1 or 2 minutes until brown fumes appear and the reaction has subsided. Then add 10 cc. of concentrated nitric acid and continue heating for about 15 minutes or until the rubber is nearly entirely dissolved. Add 10 cc. of a 60 per cent solution of perchloric acid and heat until dense white fumes appear and the solution (in the absence of insoluble

inorganic compounds) is clear and colorless. Allow to cool somewhat and slowly add 5 cc. of concentrated hydrochloric acid, once more heat until white fumes appear, cool, and wash into a 250-cc. beaker. If the solution is not perfectly clear and free from sediment it should be filtered. Dilute with distilled water to about 200 cc., precipitate the sulfur as barium sulfate in the usual manner, and weigh. If the sample contains free carbon, the free carbon need not be completely oxidized and may be filtered off after diluting. If an insoluble inorganic material is found and the presence of barium sulfate is suspected, this should be filtered off, dried, fused with sodium carbonate, and examined for sulfates.

### Combined Sulfur

The sulfur which is left in the rubber sample after extraction with acetone is usually considered as the combined sulfur. It may be determined directly on the extracted sample by the perchloric acid method described for total sulfur or may be computed as the difference between the total and free sulfur.

Combined sulfur is valued as a measure of the degree of vulcanization of a rubber stock and is frequently considered as a measure of the sulfur which has actually combined with the rubber. In most stocks, however, this is only partly true, for the combined sulfur figure would include sulfur which had been changed into or added as sulfides or other inorganic sulfur compounds. A very careful consideration of the compound and method must be made in interpreting combined sulfur values.

The T-50 test, described in a previous paper (6) is a reliable measure of state of cure and may be correlated with the true combined sulfur value of any latex compound that can be stretched considerably.

### Copper

The determination of copper and manganese in latex and compounding materials should be made occasionally. Traces of both of these elements are troublesome and cause poor aging, but quantities of either element up to 0.0015 per cent will do no harm.

Sodium dimethyldithiocarbamate is a very satisfactory reagent for determining copper. It is very sensitive and if the details listed below are followed, iron and other usually occurring elements do not interfere.

Weigh about 10 grams of the dry film into a 150-cc. beaker, and ignite in a muffle at about 400° C. to a white ash. Cool and take up the ash with about 1 cc. of hydrochloric acid and a drop of concentrated nitric acid. Evaporate to dryness on a water bath and take up with distilled water.

Treat the aqueous solution with 2 grams of citric acid and a drop of phenolphthalein, and add ammonia until a red color is produced. To this solution add 10 cc. of a 0.1 per cent aqueous solution of sodium dimethyldithiocarbamate, and extract the brown solution with successive small portions of carbon tetrachloride until the extract is only faintly yellow.

After the copper has been extracted add 1 cc. of the standard

copper solution (1 cc. = 0.0001 gram of copper) to the extracted liquid, and extract the color thus produced with carbon tetrachloride, the extract being used as the comparison standard.

A blank determination on all materials must be run in exactly the same way as the sample.

The color of the extract from the sample is compared with the standard in Nessler tubes or a colorimeter, and the amount of copper estimated. The blank is also compared with the standard, the copper in the blank subtracted from the copper found in the sample, and the difference reported as per cent of copper on the original latex solids.

After the color has been developed and extracted, it is important that the solution not be left for a long time before comparison is made, as the color fades slowly.

Sodium diethyldithiocarbamate (?) may be used equally well.

### Manganese

The periodate method for manganese has given more reliable results in the author's laboratory than either the persulfate or bismuthate methods.

Weigh about 10 grams of the latex film into a large porcelain crucible and ash in a muffle furnace at as low a temperature as possible.

Add 5 to 15 grams of potassium bisulfate to the ash (depending on how much ash is present) and fuse cautiously until effervescence ceases, then put into the muffle at moderately low red heat, and fuse until the carbon particles are burned off.

Cool, dissolve in 80 cc. of 5 per cent sulfuric acid, filter if necessary, add 5 cc. of 85 per cent  $H_3PO_4$ , and 0.5 gram of periodic acid, and heat until the color appears, boiling 15 minutes thereafter. Cool, dilute to 100 cc. in a volumetric flask, and compare with a standard in a colorimeter or Nessler tubes.

The standard solution is prepared by diluting carefully standardized 0.05 *N* potassium permanganate to such a volume as to contain 0.02 mg. of manganese per cc. with distilled water which has been slightly acidified with sulfuric acid, boiled with a little periodic acid, and then cooled.

### Starch

Starch may be detected in latex compounds by acidifying with hydrochloric acid and then adding a solution of iodine in potassium iodide. A blue or black coloration indicates starch.

Starch may be quantitatively determined by the following procedure:

Weigh 15 grams of the sample into a 500-cc. Erlenmeyer flask fitted with a glass condenser tube. Add 100 cc. of distilled water and 4 cc. of *N* sodium hydroxide and heat the mixture on a water bath, with air being blown over the surface until the ammonia is removed. Then cool the mixture and add water to replace any that may have evaporated. Add 20 cc. of concentrated hydrochloric acid rapidly while swirling the flask. This prevents the latex from coagulating to a solid mass. Add 40 cc. of 95 per cent alcohol and 60 cc. of benzene, attach the flask to the condenser, and allow to reflux at gentle heat for 2 hours. Refluxing for longer periods was found to give lower results.

Remove the condenser and evaporate the benzene and alcohol by blowing air over the surface of the mixture on a steam bath. Decant the clear water layer, wash the rubber residue several times with hot water, and combine the washings with the extract. Add 10 per cent potassium hydroxide solution to bring to neutrality and then bring just on the acid side with hydrochloric acid. Evaporate to a smaller volume if necessary, and make up to volume in a volumetric flask of such a capacity that a 25-cc. aliquot will yield between 15 and 500 mg. of cuprous oxide on oxidation. A precipitate of about 100 mg. of cuprous oxide is most conveniently handled. Direct boiling of the solution containing the sugar over an open flame is to be avoided, as this decomposes some of the sugar and causes low results.

The dextrose in the extract is determined by Allihn's gravimetric method as follows:

**REAGENT.** Allihn's modification of Fehling's solution, prepared by mixing, immediately before use, equal volumes of (a) and (b).

(a) Copper sulfate solution: Dissolve 34,639 grams of copper sulfate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) in water and dilute to 500 cc.

(b) Alkaline tartrate solution: Dissolve 173 grams of Rochelle salt and 125 grams of potassium hydroxide in water and dilute to 500 cc.

**DETERMINATION.** Place 30 cc. of the copper sulfate solution, 30 cc. of the alkaline tartrate solution, and 60 cc. of water in a 250-cc. beaker, cover with a watch glass, and heat to boiling. From a pipet add 25 cc. of the material to be examined, and boil for exactly two minutes, keeping the beaker covered. Filter immediately through an asbestos Gooch, wash thoroughly with water at  $60^\circ \text{C}$ ., once with acetone, and dry at  $100^\circ \text{C}$ . for 30 minutes.

The weight of dextrose corresponding to the weight of cuprous oxide may be obtained by referring to Allihn's sugar table (1, 3). The factor for converting dextrose to starch is 0.90. The weight of cuprous oxide may be converted to weight of dextrose or starch by multiplying by a factor, which varies with the weight of cuprous oxide and may be found by interpolating in Table I.

TABLE I. FACTOR FOR CONVERTING CUPROUS OXIDE TO DEXTROSE OR STARCH BY ALLIHN METHOD

$\text{Cu}_2\text{O}$ Weighed Mg.	Dextrose per Mg. of $\text{Cu}_2\text{O}$ Mg.	Starch per Mg. of $\text{Cu}_2\text{O}$ Mg.	$\text{Cu}_2\text{O}$ Weighed Mg.	Dextrose per Mg. of $\text{Cu}_2\text{O}$ Mg.	Starch per Mg. of $\text{Cu}_2\text{O}$ Mg.
15	0.520	0.468	150	0.452	0.407
20	0.493	0.443	200	0.454	0.409
40	0.467	0.420	300	0.457	0.411
60	0.459	0.413	400	0.468	0.421
80	0.455	0.410	500	0.478	0.430
100	0.453	0.408			

### Sediment and Sludge

Fill a 15-cc. centrifuge tube to the mark with the sample, stopper, and centrifuge. Decant the latex off, fill the tube with a 2 per cent solution of sodium oleate, shake up the sediment, and centrifuge again. Repeat until the sediment has been washed free from latex. Transfer the sediment to a weighed Gooch crucible, wash with water, dry, and weigh.

Results by methods which depend on measuring the volume of the sediment are not reliable, as they are too dependent on the time and speed of centrifuging as well as the physical nature of the sediment.

### Determination of Coagulum

Measure or weigh about 100 cc. of the sample and dilute with a 2 per cent sodium oleate solution until it has the consistency of normal latex. Cut a circular piece of 80-mesh wire screen cloth of such a size that it will fit inside a 5-cm. (2-inch) ordinary pipe union. Weigh and place tightly in the union and press down in the middle so that the upper surface will be concave. Clamp the pipe union in a vertical position. Pour the latex through the screen and wash with a 2 per cent sodium oleate solution and finally with water. Remove the screen, dry, and weigh. If a large amount of coagulum is expected a smaller sample should be used.

### Literature Cited

- (1) Allihn, F., *Z. Ver. Ruebenzucker-Ind.*, 1882, 32.
- (2) Am. Chem. Soc., Rubber Division, Committee on Methods of Analysis, *J. Ind. Eng. Chem.*, 14, 561 (1922).
- (3) Assoc. Official Agr. Chem., *Methods of Analysis*, 2nd. ed., pp. 454-7 (1924).
- (4) Australia Customs Tariff Proposals, Tariff Item No. 331D (Nov. 28, 1935).
- (5) Bolotnikov, V., and Gurova, V., *J. Rubber Ind. (U. S. S. R.)*, 10, 61-3 (1933); *Rubber Chem. Tech.*, 8, 87, 1935.
- (6) Gibbons, W. A., Gerke, R. H., and Tingey, H. C., *Ind. Eng. Chem., Anal. Ed.*, 5, 299 (1933).
- (7) Haddock, L. A., and Evers, N., *Analyst*, 57, 495-7 (1932).
- (8) Hauser, "Latex," Chapter 4, N. Y. Chemical Catalog Co., 1930.
- (9) Noble, "Latex in Industry," Chapter 10, New York, The Rubber Age, 1936.
- (10) Oldham, E. W., Baker, L. M., and Craytor, M. W., *Ind. Eng. Chem., Anal. Ed.*, 8, 41-2 (1936).
- (11) Parr, S. W., *J. Ind. Eng. Chem.*, 11, 230 (1919).
- (12) Wolesensky, E., *Ibid.*, 20, 1234 (1928).



## An Air-Bomb Aging Test for Tread Compounds

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**T**HE comparative age-resisting properties of tire tread compounds are determined in the laboratory by either oxygen-bomb or Geer-oven aging tests. The conditions under which these tests are carried out are standardized and from their results reliable predictions are made concerning the natural aging life of the tread compounds.

A few years ago oxygen-bomb aging tests, comparing first-quality tread compounds, could be satisfactorily carried out in from 39 to 48 hours, in which time the tread compound lost about 50 per cent of its original tensile. Today, largely because of the development of better antioxidants and organic accelerators, oxygen-bomb aging tests carried out under the same conditions require between 4 and 10 days to cause the same percentage loss in tensile, and the time necessary to carry out a Geer-oven aging test has been correspondingly increased. Therefore it is very desirable to develop a shorter laboratory aging test which can be correlated with the oxygen bomb or the Geer oven and which should be indicative of natural aging results.

The use of the air bomb as a laboratory method of carrying out aging tests has been previously suggested (1, 2). However, papers recognized that the conditions therein employed were too severe to permit reliable comparisons of the aging properties of tread compounds.

### Experimental Procedure

The procedure recommended by the American Society for Testing Materials, designated as D412-35T, was followed in carrying out the milling, vulcanizing, and testing of the rubber compounds described in this paper, and the D428-35T recommendations were followed in carrying out the oxygen-bomb and Geer-oven aging tests, with the exception that in both cases only two test pieces were broken instead of three, and in the case of the oxygen-bomb and Geer-oven aging tests one-half of the usual press-cured sheet was employed instead of the usual dumbbell test pieces.

The air-bomb aging conditions referred to as being too severe consist in placing the usual dumbbell test piece in a rack, and elongating 50 per cent; the rack is then placed in the air bomb, and a temperature of 260° F. (126.7° C.) and an air

pressure of 100 pounds per square inch (7 kg. per sq. cm.) are maintained for the duration of the test. These conditions were employed in carrying out the first series of tests in which the ratio of sulfur to rubber was varied. The results are shown in Figure 1.

In the second series of tests the elongation was varied between 0 and 50 per cent, the air pressure between 50 and 100 pounds per square inch (3.5 and 7 kg. per sq. cm.), and the temperature between 210° and 260° F. (98.9° and 126.7° C.).

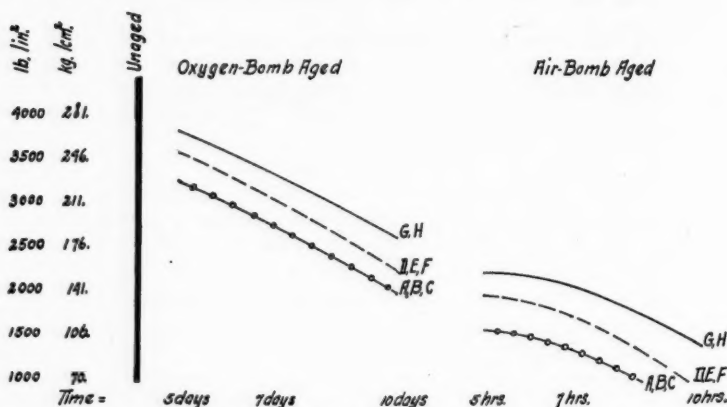


FIGURE 1. AGING TESTS

Cure, 75 minutes at 274° F. (134° C.).

Base stock: smoked sheets, 100.00; carbon black, 50.0; zinc oxide, 5.0; stearic acid, 3.0; pine tar, 2.0; antioxidant, 1.5.

Added to base stock:

	Sulfur	Accelerator		Sulfur	Accelerator
A	2.25	1.25	E	1.25	2.20
B	2.00	1.50	F	1.00	2.40
C	1.75	1.75	G	0.80	2.80
D	1.50	2.00	H	0.60	2.80

Only a single variation was made in any one test and the duration of the test was kept constant at 5 hours, as shown in Figure 2. From the data obtained in these as well as additional tests, the following conditions were adopted as more suitable for the comparing of tread compounds: elongation, 0; pressure, 50 pounds per square inch (3.5 kg. per sq. cm.); temperature, 220° F. (104.4° C.); and time, 10 hours. These "modified" conditions were employed in carrying out all the later tests shown.

In the third series of tests the oxygen concentration was varied by dilution with nitrogen. The usual dumbbell test pieces were employed here and the end point of the test was the time necessary to cause a loss of 40 per cent in tensile.

### Discussion

The results of previous laboratory comparisons of heat-resisting inner-tube compounds, which were carried out in the

air bomb, established the theory that a low ratio of sulfur to rubber was necessary (1). Therefore the first series of tests in this study was carried out to determine whether or not tread compounds with low sulfur ratios aged better than tread compounds containing normal sulfur ratios and to present data to show that these air-bomb aging conditions were too severe to permit reliable comparisons of tread compounds. The results are shown in Figure 1.

It is known that tread compounds such as those shown in Figure 1 are not practical because of their poor resistance to flex cracking and abrasion. The unaged results are not shown, but to maintain the same rate of cure for all the compounds it

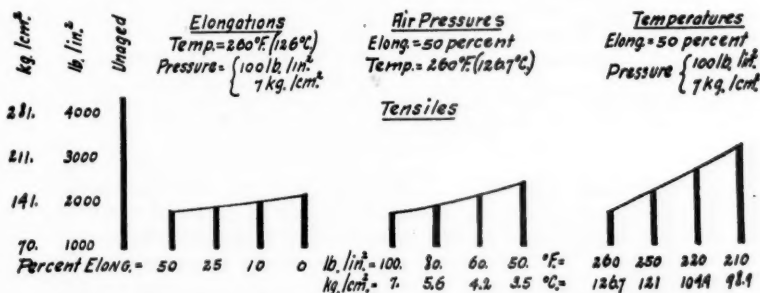


FIGURE 2. EFFECT OF VARIATIONS IN CONDITIONS OF AIR-BOMB AGING  
Cure, 60 minutes at 274° F. (134° C.) Aging time, 5 hours. Base stock: smoked sheets, 100.0; carbon black, 50.0; zinc oxide, 5.0; sulfur, 2.75; stearic acid, 3.0; pine tar, 2.0; accelerator, 1.25; antioxidant, 1.50.

was necessary to increase the accelerator ratio as the sulfur ratio was decreased. A range of cures was carried out and aging tests were made on several cures. However, the 75-minute cure at 274° F. (134° C.) was chosen to make up this chart because it was the optimum cure. The unaged tensiles of all the compounds were the same within the usual laboratory error of  $\pm 5$  per cent. The unaged modulus figures varied between about 3000 pounds per square inch (211 kg. per sq. cm.) in the case of the A compound to about 2300 pounds per square inch (161.7 kg. per sq. cm.) in the H compound. Figure 1 represents the results of the A, B, and C compounds as being alike, but actually the results shown are the averages of the three results. The same is true, in the case of the D, E, and F and the G and H compounds. This was done in order to present a clearer picture.

The results show that reducing the sulfur ratio has improved the age-resisting properties of the tread compounds in the case of both the air-bomb and the oxygen-bomb aging, the improvement being greater in the case of the air bomb. However, even the G and H compounds show a loss of about 50 per cent in tensile due to 7 hours' aging in the air bomb, whereas previous tests showed that a heat-resisting inner-tube compound lost only about 30 per cent in tensile through aging

18 hours under the same conditions (1). Therefore, these air-bomb aging conditions are too severe, and since the main difference between the composition of the heat-resisting inner-tube compounds and tread compounds *G* and *H* is the use of

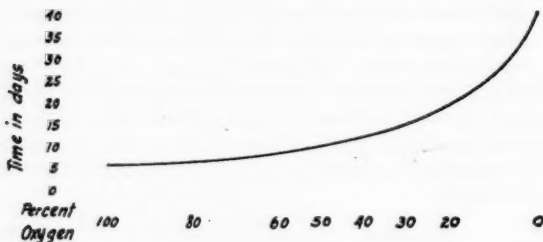


FIGURE 3. EFFECT OF OXYGEN CONCENTRATION

Same base stock as in Figure 2. End point, loss of 40 per cent of original tensile. Total pressure, 300 pounds per square inch (21.1 kg. per sq. cm.). Temperature, 158° F. (70° C.). Oxygen concentration varied from 0 to 100 per cent.

P33 black and carbon black, respectively, the conclusion seems obvious that carbon black does not age as well as some of the other compounding ingredients. Schoenfeld (5) recognized the relatively poor aging properties of carbon black and attributed them to oxygen or oxygen compounds in the carbon black.

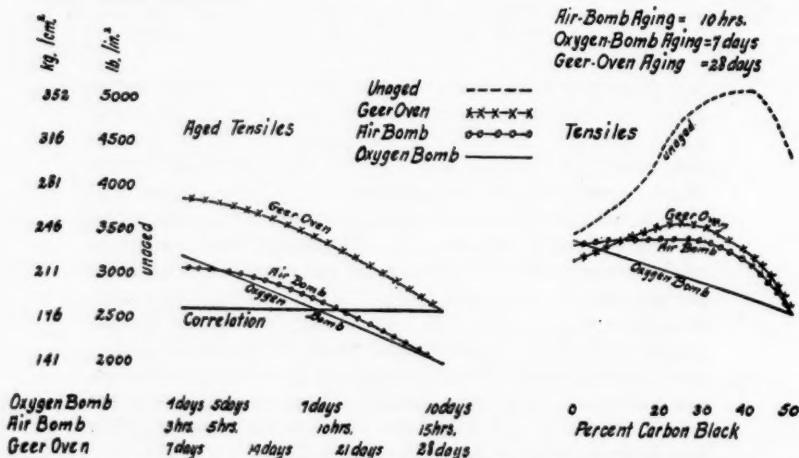


FIGURE 4. COMPARISON OF OXYGEN-BOMB, AIR-BOMB, AND GEER-OVEN AGING

Left, base stock, same as in Figure 2  
Right, same stock except carbon black varied from 0 to 50 parts  
Cure, 60 minutes at 274° F. (134° C.)

The second series of tests was carried out to determine which of the air-bomb aging conditions had the greatest effect on the results. The data shown in Figure 2 indicate that the temperature employed has the greatest effect. These results,

together with a few confirming tests, led to the adoption of the "modified" air-bomb aging conditions given above.

The compound employed here and in all the later tests is probably higher in accelerator and antioxidant ratio than is usual in commercial compounds. The accelerator employed in all the compounds in this paper is dibenzothiazyl dimethylthiol urea and the antioxidant employed is a ketone-primary aromatic amine reaction product. This compound has an excellent range of cure, showing no indications of over-cure up to the 105-minute cure. The abrasion index and flex cracking resistance are excellent. The 400 per cent modulus figure of the cure shown was about 3200 pounds per square inch (225 kg. per sq. cm.) and the tensile was about 4400 pounds per square inch (309 kg. per sq. cm.).

In the third series of tests the oxygen concentration was

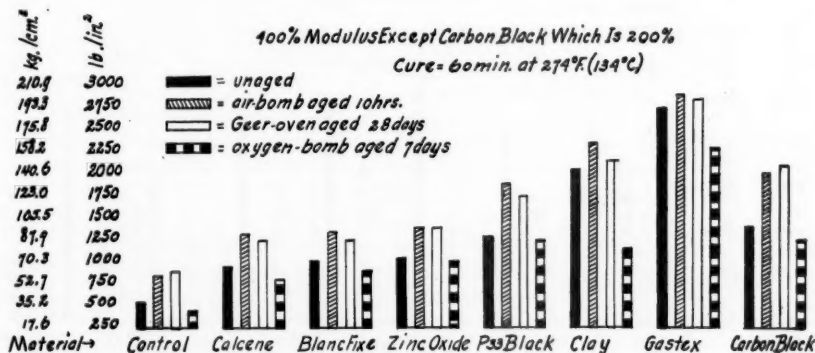


FIGURE 5. EFFECT OF COMPOUNDING INGREDIENTS

Base stock, smoked sheets, 100.00; zinc oxide, 5.0; sulfur, 2.75; stearic acid, 3.0; pine tar, 2.0; accelerator, 1.25; antioxidant, 1.50.

Added to base stock:

- A, control
- B, calcene (CaCO<sub>3</sub> plus stearic acid), 50.0
- C, blanc fixe, 50.0
- D, zinc oxide, 50.0
- E, P33 black (soft black), 50.0
- F, clay, 50.0
- G, Gastex (soft black), 50.0
- H, carbon black, 50.0

varied in an attempt to obtain data which would explain the differences between the results of the oxygen-bomb and the Geer-oven aging tests and perhaps suggest better conditions under which to carry out comparisons of tread compounds. The results are shown in Figure 3. The only obvious conclusions that can be made from these results are that a temperature higher than 158° F. (70° C.) is necessary materially to shorten the time necessary to carry out aging tests, even though the oxygen concentration is 100 per cent.

In the fourth series of tests a comparison was made of air-bomb, oxygen-bomb, and Geer-oven aging, and the results are shown in Figure 4. The "modified" air-bomb aging con-

ditions were employed in this comparison. The results show a correlation of the three aging methods. A horizontal line was drawn which represents a loss of 40 per cent in tensile (indicated as "correlation") and shows that about 10 hours' aging in the air bomb has brought about the same loss of tensile as about 7 days' aging in the oxygen bomb or 28 days' aging in the Geer oven. Realizing that many more tests must be carried out before an exact correlation of the three aging methods can be made, this apparent correlation is shown to emphasize the shorter length of time necessary to carry out air-bomb aging tests and to explain the reason for adopting these various times in carrying out later comparisons.

Also shown in Figure 4 are the results of tests to determine whether the same correlation held for various amounts of carbon black. As the carbon black content is increased from

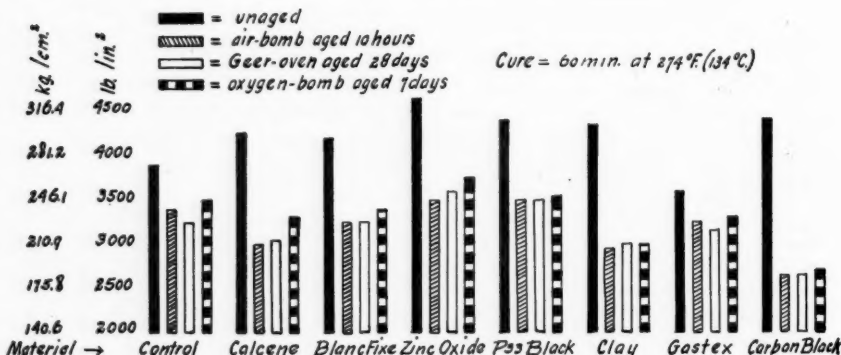


FIGURE 6. TENSILE RESULTS WITH COMPOUNDS IN FIGURE 5

0 to 50 per cent based on the rubber content, the unaged tensile increases rapidly until about 40 per cent of carbon black is present. At this point the tensile decreases rapidly. The air-bomb and Geer-oven aging also show a slight initial increase in tensile as the carbon black content is increased with a later decrease, but nevertheless the percentage loss in tensile increases progressively as the carbon black content is increased. The oxygen-bomb aging shows no increase as the carbon black content is increased. These results show that the correlation is not exact for these various aging methods when different amounts of carbon black are employed. However, the air-bomb and Geer-oven aging are probably within the limit of experimental error.

In the last series of tests a comparison was made of the effect of several compounding ingredients on the aging of rubber compounds. These results are shown in Figures 5 and 6. With carbon black it was necessary to show the 200 per cent modulus figures, because in the Geer-oven and air-



bomb aging the elongations were less than 400 per cent. Figure 5 shows the modulus results unaged and after aging in the air bomb, oxygen bomb, and Geer oven. Each compound shows an increase of the aged modulus over the unaged modulus for air-bomb and Geer-oven results, while the modulus decreases after oxygen-bomb aging. Figure 6 shows the tensile results obtained with the same compounds. These results show definitely that, irrespective of pigment used, the "modified" air-bomb aging conditions parallel the Geer-oven results, but show considerable variation from the oxygen-bomb results. In other words, the higher temperature employed for a shorter length of time in the air bomb has practically the same effect on continuing vulcanization and oxygen deterioration as is obtained in the Geer-oven tests.

### Conclusion

Data here presented demonstrate that study of tread compounds by the air-bomb aging method must include modifications of the conditions followed in the comparison of inner-tube compounds.

Data are presented which show the effect of air pressure, temperature, elongation, oxygen concentration, time, and pigment variation on the aging of rubber compounds.

The air-bomb aging conditions suggested for the study of tread compounds, consisting in testing at 0 elongation, 50 pounds air pressure per square inch (3.5 kg. per sq. cm.), and 220° F. (104.4° C.) temperature, have provided a shorter laboratory test which parallels the Geer-oven aging test in its effect on carbon black compounds.

### Literature Cited

- (1) Booth, E. W., *Ind. Eng. Chem.*, **24**, 555 (1932).
- (2) Booth, E. W., *Rubber Age* (N. Y.), **34**, 268-71 (1934).
- (3) Schoenfeld, F. K., *Ind. Eng. Chem.*, **27**, 571 (1935).

## Determination of Sulfur in Rubber

### Use of Tetrahydroxyquinone as a Titration Indicator

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and Delbert C. Cline\*\*

THE use of tetrahydroxyquinone was first suggested as an indicator for the direct titration of sulfate by Schroeder (1) and the application of the method was extended by Sheen and Kahler (2). This method allows the direct titration of sulfate in a sample with standard barium chloride solution, the end point being indicated by a change from the yellow sodium salt to the red barium salt of the tetrahydroxyquinone.

It has been necessary to determine the sulfur in rubber by gravimetric precipitation as barium sulfate, inasmuch as most rapid methods proposed up to the present time have not been found sufficiently accurate to warrant acceptance by the field. The method proposed allows for the oxidation of sulfur by standard procedures to sulfate, precipitation of the sulfate with excess barium chloride, as well as precipitation of the zinc, iron, and other heavy metals by potassium hydroxide, filtration of the precipitate, neutralization of the filtrate to the acid side of phenolphthalein, and the back-titration of excess barium ion with the standard sodium or potassium sulfate to a colorimetric end point from the red barium salt of tetrahydroxyquinone to the yellow sodium salt of tetrahydroxyquinone. This method requires only a small fraction of the time consumed in a gravimetric analysis and the accuracy is well within acceptable limits for sulfur control.

### Experimental

The indicator used throughout this study was manufactured in the Betz laboratories and considerable quantities have been furnished for the determination of sulfur in coal, oil, water, and cement, and in other fields where the determination of sulfate has previously been performed mainly by gravimetric precipitation. The indicator is a dispersion in potassium chloride of the disodium salt of tetrahydroxyquinone, ground to pass a 100-mesh screen, and is supplied under the name of THQ.

**MATERIALS AND REAGENTS.** Standard barium chloride solution, 1 cc. = 3 mg. of sulfur. Standard sodium sulfate solution,

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1 cc. = 0.8 mg. of sulfur. Hydrochloric acid, 0.02 *N*. Tetrahydroxyquinone indicator. Ethyl alcohol or ethyl denatured by formula 30, 3-A, or 2-B, or isopropyl alcohol. Freshly prepared 10 per cent solution of potassium hydroxide (carbonate-free). Phenolphthalein indicator. Measuring dipper capacity 0.2 gram of tetrahydroxyquinone.

PROCEDURE. Oxidize the sulfur from the rubber by one of the standard methods. Select a volume of the solution equivalent to a 1-gram sample of rubber and precipitate the sulfate by pipetting into the solution 50 cc. of standard barium chloride in the cold (1 cc. = 3 mg. of sulfur). (This amount of barium chloride solution will allow a sufficient excess to precipitate up to 13 per cent of sulfur in rubber. Higher percentages can be determined by using a higher excess.) Introduce phenolphthalein indicator and add 10 per cent freshly prepared potassium hydroxide just to the alkaline side of the phenolphthalein. Zinc, iron, and other heavy metals will be precipitated.

TABLE I. COMPARISON OF GRAVIMETRIC ANALYSIS AND TETRAHYDROXYQUINONE METHOD

Sample No.	Volume of $\text{Na}_2\text{SO}_4$ <sup>b</sup> Cc.	Sulfur		Difference %	Other Materials Present %
		THQ %	Gravimetric %		
1	35.20	2.02	2.02	0.00	ZnO 4.50
	35.10	2.07	2.05	0.02	
2	35.18	2.03	2.02	0.01	ZnO 10.3
	35.20	2.02	2.02	0.00	
3	35.14	2.05	2.06	0.01	ZnO 14.8
	35.18	2.03	2.03	0.00	
4	36.68	1.37	1.33	0.04	ZnO 5.5 CaO 7.5 Fe 2.6
	36.58	1.42	1.37	0.05	
5	22.04	7.81	7.87	0.04	ZnO 5.4
	22.10	7.78	7.85	0.07	

<sup>a</sup> Analyses were performed in the laboratories of W. H. & L. D. Beta.

<sup>b</sup>  $\text{Na}_2\text{SO}_4$ , 1 cc. = 0.549 mg. of sulfur.  $\text{BaCl}_2$ , 1 cc. = 3.496 mg. of sulfur.

Filter through coarse rapid paper. It will be found that a gelatinous precipitate of zinc hydroxide, etc., will occlude the precipitated barium sulfate in such a manner that a fine paper is not required. Wash the precipitate carefully with small portions of cold distilled water, keeping the volume of filtrate at a minimum. Make the filtrate up to a volume of 200 cc. in a volumetric flask and pipet 25 cc. of the total volume into a 125-cc. Erlenmeyer flask. Discharge the red color of the phenolphthalein with 0.02 *N* hydrochloric acid, add 25 cc. of alcohol (ethyl, denatured by formula 30, 3-A, or 2-B, or isopropyl) and one dipper of tetrahydroxyquinone, and titrate with standard sodium sulfate until the red color of the solution changes to a yellow. Shake the flask thoroughly during the titration to establish equilibrium conditions.

CALCULATION OF RESULTS. With the above conditions Equation 1 can be used to calculate the percentage of sulfur present in 1 gram of the original sample.

$$0.1 [150 - (\text{cc. of } \text{Na}_2\text{SO}_4 \times 0.80 \times 8)] = \text{per cent of total sulfur in rubber} \quad (1)$$

where

0.1 is a factor involving the change of mg. of sulfur to grams of sulfur and 100

150 is the number of mg. of sulfur equivalent to 50 cc. of barium chloride  
 cc. of  $\text{Na}_2\text{SO}_4$  is the volume of  $\text{Na}_2\text{SO}_4$  required in the back-titration of a 25-cc. sample  
 0.80 is the strength of  $\text{Na}_2\text{SO}_4$  in mg. of sulfur per cc. used in the back-titration  
 8 is a factor for the aliquot of the sample taken in the titration

Some of the routine work done in the application of the method to date has shown that a 0.25-gram sample gives excellent results. With this size of sample, precipitate the sulfate with 10 cc. of barium chloride (1 cc. = 7.5 mg. of sulfur), proceed as above, and back-titrate with sodium sulfate (1 cc. = 0.40 mg. of sulfur). The formula then for the total sulfur is:

$$0.4 [75 - (\text{cc. of } \text{Na}_2\text{SO}_4 \times 0.40 \times 8)] = \text{per cent of total sulfur in rubber} \quad (2)$$

In the determination of free sulfur, use the procedure advanced for total sulfur with the following modifications:

Convert the sulfur in a 2-gram sample by the customary procedure and precipitate the sulfate in the cold by introducing 20 cc. of barium chloride (1 cc. = 3 mg. of sulfur). Proceed as above with the addition of potassium hydroxide and filtration (use a fine paper, which will retain barium sulfate), making the filtrate up to 100 cc. It is possible to confine the filtrate to this volume, even after thorough washing, because of the absence of zinc, iron, etc.

The sulfur content is computed by Formula 3.

$$0.05 [60 - (\text{cc. of } \text{Na}_2\text{SO}_4 \times 0.80 \times 4)] = \text{per cent of free sulfur in rubber} \quad (3)$$

The validity of the method was established under both research and routine conditions. Under research conditions, a number of solutions were prepared in the laboratories of the Firestone Tire & Rubber Company and the method for the determination of sulfur was applied in the Betz laboratories. The results are given in Tables I and II, showing a comparison of gravimetric precipitation as barium sulfate with the results obtained with tetrahydroxyquinone. Table I gives results with total sulfur and Table II with free sulfur.

In Table I the maximum difference in the gravimetric analysis was 0.04 per cent with an average of 0.025 per cent and the greatest difference of the tetrahydroxyquinone method was 0.05 per cent with an average of 0.033 per cent. The average difference between percentage of sulfur determined by gravimetric analysis and tetrahydroxyquinone is 0.03 per cent. These percentage differences are well within the limits of 0.1 per cent as set up by the A. S. T. M.

Table II shows that the maximum difference obtained in sulfur percentage when the tetrahydroxyquinone method is compared to the gravimetric method is 0.03 per cent, while

the average percentage difference is 0.01 per cent. Here again the tetrahydroxyquinone method gives results very safely within the limits of tolerance set up by the A. S. T. M.

Under routine conditions in the Firestone Tire & Rubber Company, the total sulfur in four different types of stocks was determined by gravimetric analysis and tetrahydroxyquinone method. Five cubic centimeters of barium chloride (1 cc. = 4.110 mg. of sulfur) were used to precipitate the sulfate except in the case of sample 3, mechanical goods stock, where 6 cc. were employed. Results obtained by these two methods are presented in Table III.

Table III shows that with various types of rubber stocks the tetrahydroxyquinone method gave results within an

TABLE II. COMPARISON OF GRAVIMETRIC ANALYSIS AND TETRAHYDROXYQUINONE METHOD

(In determination of free sulfur in rubber)

Sample No.	Volume of $\text{Na}_2\text{SO}_4^a$ Cc.	Sulfur		Difference %
		THQ <sup>b</sup> %	Gravimetric <sup>c</sup> %	
1	30.88	0.100	0.106	0.006
	30.96		0.097	0.003
2	27.40	0.500	0.490	0.010
	27.52		0.480	0.020
3	22.95	0.973	0.977	0.004
	23.00		0.973	0.000

<sup>a</sup>  $\text{Na}_2\text{SO}_4$ , 1 cc. = 0.549 mg. of sulfur.  $\text{BaCl}_2$ , 1 cc. = 3.496 mg. of sulfur.

<sup>b</sup> Analysis completed in laboratories of W. H. & L. D. Beta.

<sup>c</sup> Analysis completed in laboratories of Firestone Tire & Rubber Co.

TABLE III. COMPARISON OF GRAVIMETRIC ANALYSIS AND TETRAHYDROXYQUINONE METHOD<sup>a</sup>

(In determination of total sulfur in rubber)

Sample	Volume of Na <sub>2</sub> SO <sub>4</sub> <sup>b</sup> Cc.	Sulfur		Difference %
		THQ %	Gravimetric %	
Tread stock				
1	12.70	2.63	2.61	0.02
2	13.20	2.41	2.43	0.02
3	14.80	1.71	1.67	0.04
Ply stock				
1	12.90	2.54	2.52	0.02
2	14.00	2.06	2.04	0.02
3	13.90	2.10	2.07	0.03
4	12.35	2.78	2.80	0.02
Extra tread ply				
1	12.60	2.68	2.63	0.05
2	14.40	1.88	1.87	0.01
3	13.60	2.24	2.22	0.02
4	14.20	1.97	1.98	0.01
Mechanical goods stock				
1	12.35	2.78	2.74	0.04
2	8.90	4.30	4.25	0.05
3	5.38	5.85	5.80	0.05
4	14.65	1.77	1.73	0.04

<sup>a</sup> Analyses were performed in laboratories of Firestone Tire & Rubber Co.

<sup>b</sup>  $\text{Na}_2\text{SO}_4$ , 1 cc. = 1.100 mg. of sulfur.  $\text{BaCl}_2$ , 1 cc. = 4.110 mg. of sulfur.

average of 0.03 per cent of gravimetric analysis in fifteen determinations, the greatest difference between the two methods being 0.05 per cent.

Prior to the establishment of the method as presented, a direct titration of sulfate was attempted by employing tetrahydroxyquinone after the removal of the zinc, iron, etc., which offered interference in the quantities present in these samples. Exhaustive work proved that the removal of the zinc, iron, etc., by precipitation through the addition of potassium hydroxide, potassium carbonate, trisodium phosphate, and potassium ferrocyanide over various pH ranges from 4 to 8 removed a high percentage of sulfate, probably by occlusion and the formation of the insoluble sulfate complexes. All results were low, in some cases to the extent of 50 per cent, and therefore the direct titration of sulfate was discarded and the back-titration was investigated and found to be successful.

### Conclusion

The determination of sulfur in rubber by the precipitation of oxidized sulfur as sulfate by means of barium chloride and the back-titration of the excess barium has been shown to be as accurate as the gravimetric procedure in solutions of the characteristics described above, for the determination of sulfur, with the use of tetrahydroxyquinone as the indicator. The method is very rapid compared to the gravimetric procedure and after oxidation to the sulfate form in solution, a determination can be made on a single sample in 20 to 30 minutes; with groups of analyses this time can be greatly reduced when compared to the time required for a single analysis.

### Acknowledgment

This problem was studied as a joint project by the Firestone Tire & Rubber Company, Akron, Ohio, and the W. H. & L. D. Betz laboratories, Philadelphia, Pa., and the aid of both companies is gratefully acknowledged.

### Literature Cited

- (1) Schroeder, W. C., *Ind. Eng. Chem., Anal. Ed.*, 5, 403-6 (1933).
- (2) Sheen, R. T., and Kahler, H. L., *Ibid.*, 8, 127 (1936).



## Determination of Diaryl- amines in Rubber Com- positions

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THIS paper deals with semi-quantitative methods for the determination of certain typical diarylamine age resisters—namely, diphenylamine, phenyl- $\beta$ -naphthylamine, and *N,N'*-diphenyl-*p*-phenylenediamine. It serves as an essential feature of a study of the general behavior of these materials in rubber to be discussed in a subsequent communication.

Previous methods for the detection and estimation of rubber age resisters have been of limited though of useful application. Thus Endô (3) described the colors produced by the action of sulfuric acid on a large number of commercial age resisters unmixed with rubber. Later Endô (4) published papers dealing with the action of concentrated nitric acid and Erdman reagent (solution of 0.5 ml. of concentrated nitric acid in 100 ml. of concentrated sulfuric acid) as well as of Mandelin reagent (solution of 1 gram of ammonium vanadate in 200 grams of concentrated sulfuric acid) and of concentrated sulfuric acid containing 1 per cent of arsenic acid.

Tests similar to those of Endô have been used in this laboratory. For example, a good test for the presence of *N,N'*-di- $\beta$ -naphthyl-*p*-phenylenediamine in a rubber mixture involves cutting a gram of the stock into fine pieces and covering them with concentrated sulfuric acid. After several minutes the acid layer, which is usually straw-colored, is decanted and treated with one drop of a 10 per cent mixture of concentrated nitric acid in concentrated sulfuric acid. If the diamine is present a blue color appears immediately. The presence of *N,N'*-diphenyl-*p*-phenylenediamine is attended by the formation of a red color under these conditions. This test is not vitiated by the presence of the usual quantities of diphenylamine or the phenyl-naphthylamines which may be present in the rubber. If neither a red nor a purple color is produced it is probably safe to say that less than 0.1 per cent of either diamine is present. Interfering substances sometimes produce colors with sulfuric acid alone—for example, 2,4-diaminodiphenylamine produces a deep red which changes somewhat when nitric acid is added.

Usually age resisters cause staining of the surface of light-colored stocks during cure or during aging. The colors produced, especially those arising from exposure to light, are more or less characteristic of the age resister present. Kirchhof (6) has suggested the use of metallic salts with or without exposure to light for the purpose of distinguishing certain

antioxidants, but this suggestion seems not to have been adopted. Morris (7) has published preliminary data on the fluorescent colors of several antioxidants.

Sometimes an age resister will bloom in sufficient amounts so that it can be removed, purified, if necessary, and identified by the usual qualitative methods, such as the determination of the melting point and mixed melting point with an authentic specimen. Thus *N,N'*-diphenyl-*p*-phenylenediamine, phenyl- $\beta$ -naphthylamine, *p*-phenylphenol, *p*-hydroxy-*N*-phenylmorpholine, *p*-triphenylmethyldiphenylamine, and others have been detected and identified. In a similar manner antioxidants have been recognized occasionally in the sediment from rubber cements. No one seems to have subjected rubber to very low temperatures for the specific purpose of causing age-resister bloom, although icebox temperatures have been tried occasionally. A microscope for the examination of rubber surfaces is of great help in identifying the presence of certain antioxidants.

The isolation of age resisters from rubber by extraction with solvents (1, 5) has been infrequently reported in the literature, including those which are removable from crude rubber by extraction with acetone.

At the beginning of the present work it was found possible to remove phenyl- $\beta$ -naphthylamine from rubber by extraction with acetone or with constant-boiling methanol-benzene mixture. The amine could then be steam-distilled from the dried extract or it could be precipitated from hexane or benzene solution as phenyl- $\beta$ -naphthylammonium chloride. The extracts, however, were rather intractable, and the recovery of amine was low in all experiments.

A much better method involved the steam-distillation of diarylamines from rubber. The preliminary results were successful and seem to be of sufficient interest to warrant publication. Thus it is possible to isolate such amines as phenyl- $\beta$ -naphthylamine, *N,N'*-diphenyl-*p*-phenylenediamine, and diphenylamine from rubber as the pure compounds or in the form of suitable derivatives.

### Procedures

**DETERMINATION OF PHENYL- $\beta$ -NAPHTHYLAMINE.** Aside from the removal of sulfur and other alkali-soluble materials by reaction with sodium hydroxide, the only reactions involved in this determination are the formation of the hydrochloride of the amine and the subsequent hydrolysis of the hydrochloride.

The stock is preferably either ground to pass a 14-mesh screen or is sheeted on a tight mill. For batches containing between 1 and 2 per cent of antioxidant a 30-gram sample is used, but for higher concentrations the weight can be reduced correspondingly. The 30-gram sample is refluxed with 600 ml. of water and 7.5 grams of sodium hydroxide for 2 hours. The hot mother liquor is then decanted or removed by filtering. After washing the

stock with a small amount of hot water it is refluxed with 600 ml. of water and 1 gram of sodium hydroxide. The extracted stock is then transferred to the distillation tube, A, shown in Figure 1, in the neck of which is a filter plug of glass wool. The stock is finally washed with a small amount of hot water. The tube is then submerged in the hot oil bath, D, and steam is introduced at 170° to 180° at such a rate that 4 to 4.5 liters of distillate are collected during 2.5 to 3 hours. It passes through an air condenser into a receiver cooled with water.

The distillate has a characteristic rubber-like odor. It is neutral to litmus. The suspended matter that is present is nearly colorless and contains, in addition to the anti-oxidant, a quantity of stearic acid and other material soluble in alkali, presumably fatty acids. The suspended matter is easily filtered off, especially after it has stood overnight, which is the usual practice.

For this operation a 60-mm. Büchner funnel with a No. 2 Whatman filter paper has been found convenient. When as much as possible of the water has been removed by suction, the Büchner funnel is transferred to a tared 50-ml. suction flask and the solid matter, including that deposited in the air condenser and the receiving flask, is rinsed through the funnel into the suction flask with 75 ml. of ether from a 10-ml. pipet. Much of the ether is lost through evaporation during the rinsing operation. If 0.5 cc. or more of water is collected in the suction flask, it is removed by means of a pipet and washed with a little ether, using the pipet also for this washing operation. The wash ether is then added to the suction flask and all the ether is evaporated on the steam plate. Small amounts of water can be removed by adding 10 ml. of benzene and evaporating until the benzene is removed. The last traces of water are removed by heating for 20 minutes in an oven at 120° to 130°.

The solid remaining, to be referred to as the "residue from the ether evaporation," is weighed to 0.01 gram, and dissolved in 10 to 20 ml. of warm hexane. A stream of hydrogen chloride is allowed to play for a few minutes over the surface of the solution while it cools to room temperature. The hydrogen chloride causes phenyl- $\beta$ -naphthylamine hydrochloride to precipitate as a clot that clings firmly to the bottom and walls of the flask. The precipitation is complete when the mother liquor becomes clear or has stood for 2 hours. The mother liquor is then poured into another tared flask and the hydrochloride washed with a few milliliters of hexane. The washings are united with the mother liquor and evaporated to dryness, finally, in the oven at 120° to 130° for 20 minutes. The residue, known as the "residue from the hexane evaporation," is then weighed to 0.01 gram. It contains nonbasic materials.

The flask containing the hydrochloride is quickly evacuated in a vacuum desiccator and weighed to 0.01 gram. The hydrochloride is not pure, but seems to contain traces of free hydrochloric acid and possibly traces of other difficultly volatile material. It is hygroscopic. In order to determine the phenyl- $\beta$ -naphthylamine content, the hydrochloride is hydrolyzed. This is easily done by boiling with 10 ml. of benzene and 10 ml. of water until the solid has dissolved. The water layer is then separated and washed with ether by means of a pipet. The ether washings are added to the benzene layer, which is then evaporated on the steam plate until the solvent is removed. The last traces of water are removed by heating for 20 minutes in an oven at 120° to 130°. The residue is phenyl- $\beta$ -naphthylamine, and is weighed to 0.01 gram.

A description in more detail of the apparatus shown in Figure 1 follows.

The distillation tube, *A*, is made by bending a piece of Pyrex tubing 30 cm. (12 inches) long and 4.4 cm. (1.75 inches) in outside diameter, so that it can be submerged in the oil bath, *D*. A neck made from a piece of 1.25 cm. (0.5 inch) outside diameter tubing is attached and bent so that it can be connected to the short air condenser, *E*. The thermometer well in *A* is inserted by means of a ring seal. The brass superheater, *B*, of the type sold by the Fisher Scientific Company, is fitted with a thermometer well and 0.6-cm. (0.25 inch) copper tubing connections. The steam generator, *C*, is a 20-liter (5-gallon) steel drum. Service line steam is unsatisfactory because of admixed oxygen. The still head on *C* has a bulb of 300-ml. volume. The steam generator, *C*, the superheater, *B*, and the oil bath, *D*, are heated with gas burners. The receiver, *F*, is a 5-liter balloon flask cooled with tap water. The various parts of the apparatus are connected by means of rubber tubing or rubber stoppers.

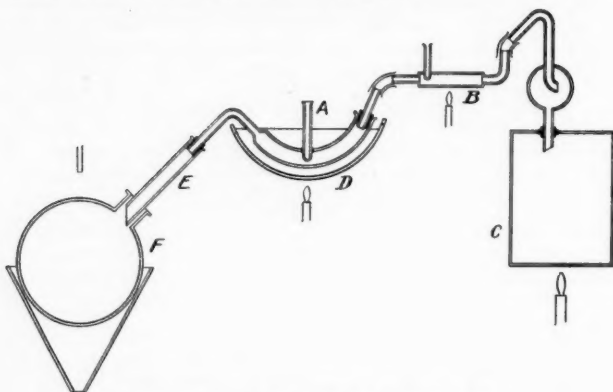


FIGURE 1. DIAGRAM OF APPARATUS

It is probable that the precision and speed of conducting the determinations would be improved by the use of small all-glass apparatus, thus making it possible to use small samples.

**DETERMINATION OF *N,N'*-DIPHENYL-*p*-PHENYLENEDIAMINE.** The procedure is the same as that for phenyl- $\beta$ -naphthylamine up to the point of the hydrochloride precipitation. Here benzene must be substituted for hexane, and benzene must be used instead of ether to wash the product into the precipitation flask.

Since the hydrochloride does not adhere well to the precipitation flask, filtration is necessary in order to separate the mother liquor. The hydrochloride is collected in the precipitation flask and hydrolyzed by boiling for several minutes with a mixture of 5 ml. of water, 3 ml. of concentrated ammonium hydroxide, and 5 ml. of benzene. The water layer is separated by means of a pipet and washed with a few milliliters of benzene. The benzene layers are united and evaporated to dryness. Finally the residue is heated for 20 minutes at 120° to 130° C. and weighed. It should melt at approximately 145°.

**DETERMINATION OF DIPHENYLAMINE.** The procedure given for phenyl- $\beta$ -naphthylamine can also be used for diphenylamine if due allowance is made for volatility and for solubility in the extracting solutions. It is more convenient, however, since diphenylamine is volatile in steam at 100°, to use a modification of Cook's method (2) for diphenylamine in smokeless powder.

A 30-gram sample of the stock, 5 grams of sodium hydroxide, and 3 liters of water are distilled in a 5-liter distilling flask until 4 liters of distillate have been collected. Water is added to the distillation flask from time to time as necessary. The diphenylamine is extracted from the distillate with three 75-ml. portions of petroleum ether. The extracts are collected in a tared 150-ml. flask and evaporated to a volume of about 5 ml. Five milliliters of ether and 8 ml. of a 10 per cent solution of bromine in carbon tetrachloride are added. The solvents are boiled off and the residue is heated in a current of air at about 80° during 20 minutes. It is then dissolved in 5 to 10 ml. of hot benzene. The benzene is removed in a current of air at about 80° and heated to constant weight at this temperature. The melting point of the residue, which is 2,2',4,4'-tetrabromodiphenylamine, should be between 178° and 185°. A low melting point usually indicates incomplete bromination, although aged rubber usually gives a product of somewhat lower melting point.

### Notes on Procedures

Several solvents were used for extracting small amounts of the diarylamines from water. Ether was objectionable because of its high solubility in water. Hexane and petroleum ether (b. p. 40° to 50°) were satisfactory for phenyl- $\beta$ -naphthylamine and diphenylamine. *N,N'*-diphenyl-*p*-phenylenediamine was usually extracted with benzene in which it is rather soluble. This amine is almost insoluble in hexane.

Diphenylamine can be isolated as the hydrochloride by a method similar to that for phenyl- $\beta$ -naphthylamine, provided ample precautions are taken to prevent loss by volatilization. Although bromination of diphenylamine gives a single derivative favorable to quantitative estimation, preliminary experiments indicated that the bromination of phenyl- $\beta$ -naphthylamine is not a satisfactory quantitative procedure because of the formation of several products.

Generally accepted values for the melting point of *N,N'*-diphenyl-*p*-phenylenediamine are in the neighborhood of 145° to 152°. During this study it was found that the compound actually has a double melting point, the first being at approximately 147° and the second at 152-153°. After recrystallization from alcohol or benzene, melting occurs at the lower temperature when the melting point tube is immersed in the previously heated bath; resolidification then takes place and, as the temperature is raised, remelting occurs at 152-153°.

In the procedure for diphenylamine the solution of the

tetrabromo derivative in benzene before drying to constant weight is not necessary although it aids somewhat in removing hydrobromic acid.

### Results and Discussion

**PHENYL- $\beta$ -NAPHTHYLAMINE WITHOUT RUBBER.** In a few leading experiments this amine was steam-distilled in the absence of rubber. At 100° the rate was too slow to be practicable, but at a higher temperature a convenient rate was obtained.

A quantity (0.50 gram) of phenyl- $\beta$ -naphthylamine was placed in the distilling tube, A (Figure 1), and 4100 ml. of distillate were collected with the temperature in A at 165° to 175°. The distillate was worked up in the usual manner except that the hydrochloride precipitation was omitted. The yield of recovered phenyl- $\beta$ -naphthylamine was 0.49 gram. It melted at 108–109°. The filtrate (4000 ml.) was extracted with 100 ml. of hexane and then with 50 ml. of hexane. A large rubber stopper was used to close the flask during extraction. The hexane extracts were united and evaporated to dryness, leaving an oily residue of 0.0306 gram. Solution of this in 5 ml. of hexane and treatment with hydrochloric acid gave 0.0049 gram of precipitate from which no phenyl- $\beta$ -naphthylamine could be isolated by treatment with benzene and water in the usual way.

**PHENYL- $\beta$ -NAPHTHYLAMINE FROM HIGH-GUM STOCK A.** A sheet of stock A, cured 70 minutes at 126.67° C. (260° F.), was used. The recipe for stock A is:

High-Gum Stock A	
Rubber	100
Phenyl- $\beta$ -naphthylamine	1
Zinc oxide	2
Stearic acid	2
Accelerator	0.3
Sulfur	1.25
	<hr/> 106.55

On milling, a crumbly sheet resulted and a 20-gram sample was analyzed in the usual way except that the steam-distillation was conducted at 165–170°.

	Gram
Residue from ether evaporation	0.27
Weight of hydrochloride	0.22
Residue from hexane evaporation	0.08
Yield of phenyl- $\beta$ -naphthylamine (m. p. 107–108°)	0.17

The yield of 0.17 gram of phenyl- $\beta$ -naphthylamine represents a recovery of 90.5 per cent of that added to the stock.

When 3 liters of the filtrate from this experiment were extracted with 100-ml. and 50-ml. portions of petroleum ether, and the extracts united and evaporated, a residue of 0.015 gram remained. This residue was oily and gave a few crystals when seeded with phenyl- $\beta$ -naphthylamine. However, when dissolved in 10 cc. of hexane and treated with hydrochloric acid, a precipitate weighing less than 0.005 gram resulted. On boiling with water and benzene no phenyl- $\beta$ -



naphthylamine could be isolated. From this it is certain that the amount of phenyl- $\beta$ -naphthylamine remaining dissolved in the filtrate from the distillate is less than 0.0017 gram per liter.

PHENYL- $\beta$ -NAPHTHYLAMINE FROM TREAD STOCK APPLIED BY DIPPING. The stock used had the following composition:

Tread Stock B	
Rubber	100
Sulfur	3
Mercaptobenzothiazole	1
Stearic acid	4
Zinc oxide	5
Gas black	50
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A sheet of this stock cured 80 minutes at 128.89° C. (264° F.) was divided into two equal parts. Each part was cut into strips approximately 2.5 × 10 cm. (1 × 4 inches), and weighed 37 grams. The following procedure was used for both parts in order to test the reproducibility of the experiments. The 37 grams of strips were immersed for 10 minutes in a solution prepared from 7 grams of phenyl- $\beta$ -naphthylamine and 70 ml. of benzene-methanol constant-boiling mixtures. After draining the solution from the strips, the solvent was evaporated and the weight of residue determined. This residue represents the unabsorbed phenyl- $\beta$ -naphthylamine. The strips which were covered with a layer of powdery phenyl- $\beta$ -naphthylamine were cut up into small pieces about 2.5 × 0.15 × 0.023 cm. (1 × 0.063 × 0.093 inch) in size. They were then introduced into the steam-distillation tube and steam-distilled in the usual way but with the omission of alkali extraction.

Table I summarizes the data for both parts of stock used.

TABLE I. TESTS ON TREAD STOCK B

	First Part		Second Part	
	Grams	Melting Point ° C.	Grams	Melting Point ° C.
Total phenyl- $\beta$ -naphthylamine in solution	7.00	108-109	7.00	108-109
Phenyl- $\beta$ -naphthylamine unabsorbed	6.79	106-108	6.80	106-108
Residue from ether evaporation	0.83	...	0.87	...
Phenyl- $\beta$ -naphthylamine after hydrochloride precipitation and hydrolysis	0.25	104-107	0.24	104-107
Phenyl- $\beta$ -naphthylamine unabsorbed plus that absorbed	7.04	...	7.04	...

It can be seen from Table I that the results for the two parts check nicely but that the amounts of phenyl- $\beta$ -naphthylamine accounted for are somewhat high. This can be explained as being due to impurities in the recovered phenyl- $\beta$ -naphthylamine indicated by the low melting points. The low melting point of the phenyl- $\beta$ -naphthylamine recovered by the steam-distillation indicates the possible presence of thiophenyl- $\beta$ -naphthylamine formed by reaction with free sulfur.

PHENYL- $\beta$ -NAPHTHYLAMINE FROM TREAD STOCK B INCORPORATED BEFORE VULCANIZATION BY MILLING. Table II summarizes the results for phenyl- $\beta$ -naphthylamine for an

undercure and an overcure, and indicates that the per cent recovery of antioxidant is not dependent to any great extent on the time of cure. If the amount of amine recovered is measured by the weight of hydrochloride and the equivalent weight of amine calculated on the basis of one molecule of hydrochloric acid and for each amine molecule, the results will be too high, owing to difficultly volatile impurities. If the weight of residue from the hexane evaporation is added to the weight of phenyl- $\beta$ -naphthylamine in each case, the value approaches the weight of residue from the ether evaporation. The material in the residue from the hexane evaporation is partly soluble in dilute sodium hydroxide and consists in part of stearic acid. Fatty acids could arise from the hydrolysis of soaps or glycerides during the steam-distillation. The reproducibility of the recovery of antioxidant is believed to be within 5 per cent.

It was of interest to test the steam-distillation of the ground stock before alkali-extracting it. The determination for the 20-minute cure of tread stock B containing 3 per cent of age

TABLE II. STEAM-DISTILLATION RECOVERY OF PHENYL- $\beta$ -NAPHTHYLAMINE FROM TREAD STOCK B

(Cured at 264° F.)

Time of Cure Min.	Weight of Sample Grams	Amine Added on the Rubber %	Amine Present in Sample Gram	Residue from Ether Evaporation Gram	Hydrochloride Yield		Recovery of Amine		Residue from Hexane Evaporation Gram
					Gram	Amine Equivalent	Gram	%	
20	30	1	0.183	0.25	0.18	0.16	0.15	82	0.11
	30	2	0.364	0.39	0.36	0.31	0.29	79	0.10
	20	3	0.362	0.38	0.35	0.30	0.28	76	0.09
160	30	1	0.183	0.28	0.17	0.15	0.14	76	0.12
	30	2	0.364	0.43	0.36	0.31	0.28	76	0.14
	20	3	0.362	0.39	0.36	0.31	0.26	71	0.11

resister on the rubber was therefore repeated omitting the extraction. The residue from the ether evaporation weighed 0.99 gram and on treatment with hexane in the usual manner not quite all of this dissolved. Dry hydrochloric acid was passed into the flask. The yield of hydrochloride amounted to 0.41 gram. On hydrolysis in the usual way 0.32 gram of crude phenyl- $\beta$ -naphthylamine resulted (m. p. 103-106°). From the rather turbid hexane mother liquor when allowed to stand overnight there was precipitated 0.05 gram of solid which was thoroughly washed with benzene. The crystals remaining were identified as sulfur by melting point (115-118°) and mixed melting point (117-119°) with an authentic specimen. Not only does free sulfur steam-distill from rubber but undoubtedly it begins to react with the antioxidant at 170-180°, thus justifying the alkali-extraction previous to the steam-distillation.

*N,N'*-DIPHENYL-*p*-PHENYLENEDIAMINE INCORPORATED BEFORE VULCANIZATION BY MILLING. High-gum stock C

which was used in some of the experiments had the following composition: Optimum cure was 60 minutes at 125.56° C. (258° F.).

High-Gum Stock C	
Rubber	100
Stearic acid	1
Sulfur	3
Zinc oxide	2
Tetramethyl thiuram disulfide	0.1
	<hr/> 106.1

Table III shows the recovery of antioxidant from tread stock B (cured 160 minutes at 128.89° C., 264° F.) and high-gum stock C (cured 60 minutes at 125.56° C., 258° F.) in per cent of that added.

DIPHENYLAMINE INCORPORATED BY MILLING. The results for tread stock B (cured 160 minutes at 128.89° C., 264° F.) and high-gum stock C (cured at 125.56° C., 258° F.) are shown in Table IV.

The volatility of diphenylamine probably explains the relatively low recovery from the stocks containing 3 per cent of diphenylamine. When tread stock B, originally containing 3 per cent of diphenylamine on the rubber, was allowed to stand in the ground condition for 10 weeks and then analyzed, a recovery of only 72 per cent was obtained. The recovery of 80 per cent, shown in Table IV, was obtained shortly after mixing and curing.

APPLICATION OF METHOD TO OTHER HIGH MOLECULAR WEIGHT MATERIALS. It has been recorded in the literature that phenyl- $\beta$ -naphthylamine is active in controlling the polymerization of chloroprene. In order to see if the commercial polymer contained this antioxidant, a sample of Duprene was sheeted out on the mill.

A 40-gram sample was wrapped in cheesecloth and steam-distilled at 170–180°. During this time considerable amounts of acid were evolved and the cheesecloth was badly decomposed. The distillate, which was oily, was extracted first with 100 ml. and then with 50 ml. of hexane. The extracts were united, evaporated to dryness, and the residue was analyzed in the usual way for phenyl- $\beta$ -naphthylamine. The amount recovered was 0.10 gram, corresponding to 0.25 per cent on the Duprene. It melted at 105–107° alone and at 106–109° when mixed with an authentic specimen.

A stock similar in composition to tread stock B with mercapto-benzothiazole omitted and with the rubber replaced by polyisobutylene (molecular weight, approximately 100,000) was used with 1 per cent of phenyl- $\beta$ -naphthylamine based on the polyisobutylene. When this stock was analyzed in the usual way, sulfur appeared in the distillate and the recovery of phenyl- $\beta$ -naphthylamine amounted to 55 per cent. In this case the amine was separated from the sulfur by hexane extraction before precipitation with hydrogen chloride. The amine recovered melted at 100–104° and probably contained some thiophenyl- $\beta$ -naphthylamine formed by reaction with sulfur not completely removed by alkali extraction.

TABLE III. RECOVERY OF ANTIOXIDANT

Concentration of Antioxidant on Rubber	Recovery of Antioxidant	
	Tread stock B	High-gum stock C
	%	%
0.5	16	65
1.0	44	83
3.0	64	85

TABLE IV. RECOVERY OF ANTIOXIDANT

Concentration of Antioxidant on Rubber	Recovery of Antioxidant			
	Tread stock B	30 min.	60 min.	120 min.
	%	%	%	%
0.5	85	87	89	93
1.0	90	..	91	..
3.0	80	..	78	..

The procedures outlined have been used in analyzing factory stocks for age resisters. They have many times been found useful in clearing up questions as to the identity of certain stocks. Other applications, such as those relating to the behavior of age resisters during aging, will be treated in a subsequent communication.

#### Literature Cited

- (1) Bruson, Sebrell, and Vogt, *Ind. Eng. Chem.*, **19**, 1187 (1927).
- (2) Cook, *Ibid.*, Anal. Ed., **7**, 250 (1935).
- (3) Endô, *J. Soc. Chem. Ind., Japan*, **38** (suppl. binding), 618 (1935).
- (4) *Ibid.*, **39** (suppl. binding), 11, 12 (1936).
- (5) Garner, *Trans. Inst. Rubber Ind.*, **4**, 413 (1929).
- (6) Kirchhof, *Kautschuk*, **7**, 7 (1931).
- (7) Morris, *Ind. Eng. Chem.*, **26**, 107 (1934).